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# Improvement of Mechanical Properties by a Polydopamine Interface in Highly Filled Hierarchical Composites of Titanium Dioxide Particles and Poly(vinyl butyral)

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**Abstract:** In this work, the preparation and properties of hierarchical composites of titanium dioxide (TiO<sub>2</sub>) particles (rutile modification) and poly(vinyl butyral) (PVB) are discussed. The volume fraction of the ceramic particles was approximately 60%. Two types of composites with different fillers were examined, i.e. TiO<sub>2</sub> particles with and without a thin coating of polydopamine (PDA). A variety of characterization methods was applied in order to analyze the properties of the particles and the composites. Infrared spectroscopy is used to verify the functionalization of the particles with a thin polydopamine layer. Thermal analysis provides information on the thermal stability and the degree of functionalization of the coated particles and the composites. Scanning electron microscopy investigations reveal that the functionalized TiO<sub>2</sub> particles with PDA form larger agglomerates which enable the coating of the TiO<sub>2</sub> particles with PVB *via* the spouted bed technique. Nanoindentation experiments show that the final hierarchical composite material with the use of non-coated TiO<sub>2</sub> particles exhibits a hardness of  $0.75 \pm 0.04$  GPa and a Young's modulus of  $29.5 \pm 1.0$  GPa. The composites containing polydopamine coated TiO<sub>2</sub> particles show an increase of

approximately 40% in hardness and 25% in Young's modulus in comparison to the composites with uncoated TiO<sub>2</sub>.

**Keywords:** Polydopamine; TiO<sub>2</sub> particles; Particle coating; Highly filled polymer composites; Spouted bed; Hierarchical materials; Nanoindentation

## 1 Introduction

Composite materials are of large technological relevance due to the combination of different material properties which can lead to a material with desired properties. In everyday life a variety of composite materials can be identified, for example concrete, car tires, plywood as well as lightweight composite constructions, [1, 2] dental fillings, [3] special coatings, [4] and membranes. [5] The material combination can vary, but one of the most common examples is the combination of ceramic or metallic particles with a polymer. These composites can be categorized in different ways. For example, one can distinguish between composites containing particles with at least one dimension being 100 nm or smaller, the so called nanoparticles, [6-8] and composites containing particles in the micrometer range in all dimensions. [9, 10] Furthermore, the degree of filling strongly affects the end-use properties of composites. On one side are nanocomposites where the polymer is the minor component [11] and the nanocomposites where the polymer is the major component. [12, 13] In both cases the polymer phase preferably forms the matrix, although percolation of the nanoparticles occurs for highly filled composites. [11, 14] Polymers often are ductile materials and characterized by a good processability at moderate temperatures, which simplifies processing. [15] Nowadays, the development of tailored composite materials is one of the most relevant research fields in material science.

In this context, one of the most crucial problems is the construction of composite materials with superior mechanical properties. Polymers, metals and ceramics exhibit different mechanical properties, so the aim is always to combine the different materials in order to obtain tailored properties. In nature a variety of natural composite materials exists, such as wood which consists mostly from cellulose and lignin as well as bones which consist mainly from hydroxyapatite and collagen. An example of a natural composite with exceptional mechanical properties is nacre. [16-19] Nacre can be found in a variety of mussels. Originally, nacre is a composite consisting of aragonite and a mixture of chitin and other biopolymers, with the aragonite particles layered arranged, glued with the biopolymer

mixture, leading to an hierarchically structured material. The hierarchical structure influences the mechanical properties. Studies on nacre indicated a Young's modulus of approximately 70 GPa. [19] It is important to mention that these types of nanocomposites have a low content of the organic phase, maintaining the ceramic stiffness and benefit from the small polymer content by an increase of ductility and a decrease of brittleness.

In order to achieve hierarchical composites, *in vitro* fabrication of nanocomposites is currently under investigation. [20] Nature inspired synthesis of composite materials is achieved through synthesis of biopolymers or oligomers such as polydopamine, chitin – chitosan or oleic acid and their combinations with other materials such as ceramic nanoparticles. [6, 21] Mussel-inspired synthesis of polydopamine is a widely known way for the fabrication of composites with the aim to achieve properties of natural composite materials. The surface modification with bio-inspired polydopamine coatings became fundamentally important in the last years. [22-24] The coating with polydopamine occurs through oxidative polymerization of dopamine hydrochloride in a buffer solution under slightly basic conditions (pH~8.5). The structure of polydopamine inherently is not understood. However, it is used for the coating of surfaces with different properties. [25] In nature biomineralization of ceramic particles and low molecular weight biopolymers or oligomers leads to the fabrication of exceptional composite materials (*e.g.*, nacre) with well-defined structure. [26] In that term, functionalization of ceramic particles *via* the mussel inspired coating of polydopamine followed by an additional coating with a polymer could lead to composites with good mechanical properties.

In this work TiO<sub>2</sub>-particles were functionalized in the first hierarchical level with polydopamine. The functionalization led to agglomerates which were additionally coated in the second hierarchical level with poly(vinyl butyral). For a uniform coating in the second hierarchical level, which is important for structural homogeneity of composites, only a few techniques can be applied. The spouted bed technique is one of the most widely used methods [27, 28] for coating of a variety of particles with a thin polymer layer. Furthermore, spouted beds are well suitable for fabrication of hierarchical materials; therefore coating of granules which are already coated with another polymer is possible. [29] During the process a great advantage is the high evaporation rate of solvents, which is typical for spouted and fluidized beds. [30] An example of the successful fabrication of hierarchical composite materials using the spouted bed technique on the second hierarchical level is the work of Brandt et al. [29] In their work TiO<sub>2</sub> particles with a diameter in the sub-micron range were coated with poly(methyl methacrylate) on a first hierarchical level *via* emulsion polymerization, and

subsequently coated with poly(vinyl butyral) to create a second hierarchical level in a spouted bed. The spouted bed technique can be applied to prepare highly filled polymer composites with large values of the reinforcement factor above the glass transition temperature of the polymer phase. [11, 31] The thermal, rheological and dielectric properties of such highly filled systems provide important information about the dynamical behavior of the polymer chains in the composites and indicate the importance of the filler-filler interaction for dynamic moduli of the composite. [11]

The objective of this work is to present another approach in biomimetic hierarchical composite fabrication as well as to show the development of hierarchical materials with exceptional mechanical properties *via* a mussel-inspired technique. More in detail, the fabrication of hierarchical composites consisting of poly(vinyl butyral) and titanium dioxide (TiO<sub>2</sub>) particles (rutile modification) is described. The volume fractions of the polymer and the ceramic particles were 40% and 60%, respectively. Two different types of composites were examined, one type with the use of TiO<sub>2</sub> with the mussel-inspired coating of polydopamine and another one without the polydopamine coating. The materials used as well as the composites were studied with FT-IR spectroscopy, thermal analysis, rheological methods, scanning electron microscopy as well as mechanical analysis *via* nanoindentation.

## **2 Experimental**

### **2.1 Materials**

The coating of TiO<sub>2</sub> particles with polydopamine was accomplished using dopamine hydrochloride (Sigma-Aldrich, Schnellendorf, Germany) and a Tris-buffer solution which was prepared using 21.81 g of Trizma<sup>®</sup> base (Sigma-Aldrich, Schnellendorf, Germany, 99.9%), 7.08 g of tris-hydrochloride (Sigma-Aldrich, Schnellendorf, Germany, 99.0%) and 15 L deionized H<sub>2</sub>O (Millipore, 0.055  $\mu$ S/cm). The pH value of the Tris-buffer solution was 8.5. Approximately 350 g Sachtleben RDI-S alumina - organic surface treated TiO<sub>2</sub> particles (Sachtleben-Chemie GmbH, Duisburg, Germany), kindly provided by the company, were used as received. According to the product information the TiO<sub>2</sub> content was 95% with a mean crystal size of approximately 200 nm and median diameter  $d_{50}$ =195 nm, measured by Zetasizer Nano ZS (Malvern Instruments Ltd, Grovewood, UK). The polymer chosen for the composites was poly(vinyl butyral) 30H from Mowital (PVB), kindly supplied by Kuraray Specialties Europe GmbH (Frankfurt am Main, Germany). The molecular characteristics of the used PVB are presented in Table 1 as reported in previous work. [11] This poly(vinyl butyral) type is a polymer that is hydrophilic since it contains 18 – 21 wt% OH groups

according to the producer (26.2 – 30.2 mol%). Ethanol (Merck, Darmstadt, Germany, 99.5%) was used as solvent - dispersion mean for the fabrication of the composites and the cleaning of the coated particles.

## **2.2 Functionalization of TiO<sub>2</sub> particles with polydopamine**

For the coating of the particles with polydopamine approximately 350 g TiO<sub>2</sub> particles were suspended in 15 L of Tris-buffer (pH=8.5), as it is described elsewhere. [24] The concentration of the TiO<sub>2</sub> particles in the suspension was approximately 20 g/L. The suspension was homogenized by rigid stirring and an ultrasonic needle apparatus (Bandelin, Berlin, Germany). After homogenization of the suspension, 30 g of dopamine hydrochloride were added and let to react for 24 h under rigorous stirring in air atmosphere. Following that, the functionalized particles were left to precipitate for 60 h. The supernatant solution of free polydopamine particles in water-buffer solution was removed while the particles were cleaned thoroughly with centrifugation at 11000 rpm. In order to remove the free polydopamine particles the coated particles were re-dispersed five times in deionized water and two times in absolute ethanol. After re-dispersion the samples were collected after centrifugation. Finally the functionalized nanoparticles were dried over several days at approximately 100 °C under vacuum in order to remove any residual solvents and kept under vacuum to avoid water uptake. In Figure 1 the synthesis of polydopamine by the oxidation polymerization of dopamine as well as the coating of the TiO<sub>2</sub> nanoparticles is presented. Since the synthesis of polydopamine is up to date not completely understood, the variety of reported possible units such as dihydroxyindole, indoleione and dopamine are presented in Figure 1. [25] It should be noted that polydopamine is a coating that is directly formed on the surface of the TiO<sub>2</sub> nanoparticles. Therefore it is not possible to perform molecular characterization and to identify the molecular weight as well as the molecular weight distribution. Additionally a variety of ways for the linking of polydopamine on TiO<sub>2</sub> nanoparticles can be hypothesized, either from the amine group or from the hydroxyl groups. In case of iron oxide particles the adhesion of the polydopamine takes place through the amine groups. Therefore it is suggested that in case of the TiO<sub>2</sub> nanoparticles the amine group of the polydopamine also links to the surface of the particles. [32] Nevertheless, Yu et al. reported the adhesion of the mussel proteins for low pH values through the OH groups of the polydopamine unit. [33] In both cases there are characteristic chemical groups (O-H, N-H) available to form a variety of covalent and/or hydrogen bonds with the surface of the particles.

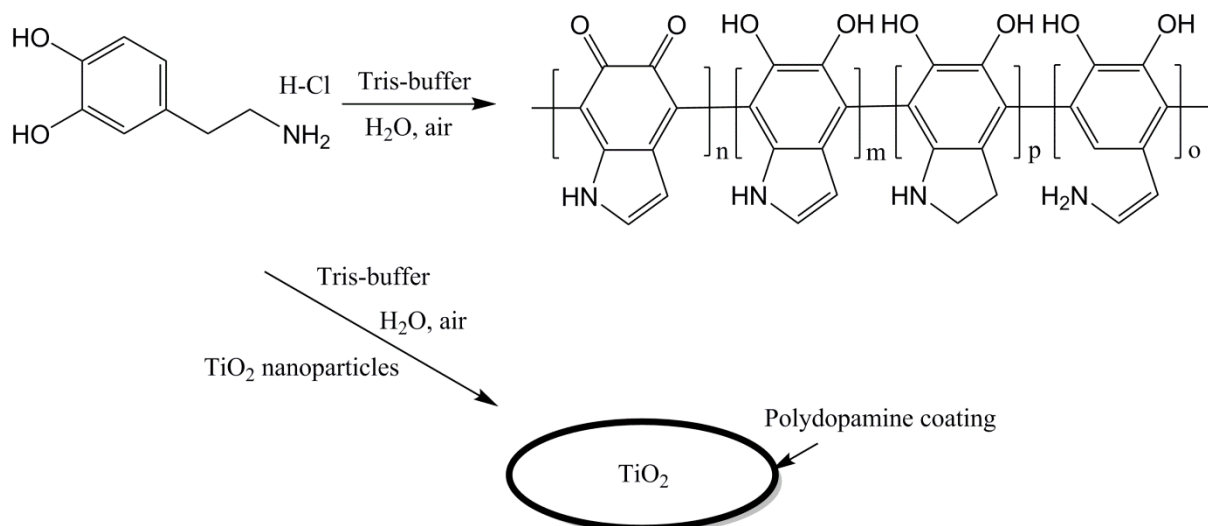


Figure 1: Oxidative polymerization of dopamine under air and functionalization of the TiO<sub>2</sub> nanoparticles with polydopamine. The different possible structures of polydopamine are presented as described in literature [25].

### 2.3 Fabrication of the hierarchical composites

The functionalized nanoparticles partially tended to agglomerate. The TiO<sub>2</sub> particles coated with polydopamine (TiO<sub>2</sub>@PDA) agglomerates were milled to granules with a diameter between 20 to 40 μm which are used as the first hierarchical level. These granules were used as feed for fabrication of second hierarchical level composites through the spouted bed spray granulation process. About 180 g of the TiO<sub>2</sub>@PDA granules were set in the spouting state in the apparatus at a gas flow (ambient air) of 15-25 m<sup>3</sup>/h. Before entering in the process chamber of the spouted bed process, the used gas was preheated and the temperature in the process chamber was kept between 30 and 40 °C. For the granulation of TiO<sub>2</sub>@PDA-granules, poly(vinyl butyral) Mowital 30H was used. Poly(vinyl butyral) was dissolved in ethanol with a concentration of 4 wt%. The solution was sprayed into the spouted bed with a spraying rate of approximately 5 g/min. During the granulation process TiO<sub>2</sub>@PDA-granules with a diameter between 20 to 40 μm were coated and partially agglomerated. The partial agglomeration cannot be completely avoided in the processing of fine particles. As a result, the agglomerates of TiO<sub>2</sub>-particles functionalized with polydopamine and coated with poly(vinyl butyral) (PVB-TiO<sub>2</sub>@PDA) were formed with a diameter between 40 and 200 μm. After the granulation process, the agglomerates were hot-pressed for 1 hour at a temperature of 160 °C and a pressure of 750 MPa using an automatic press PWV 300 (Paul-Otto Weber GmbH, Remshalden, Germany). After pressing, the compact was grinded to get a smooth surface. The fabricated composite was cut into

specimens with a rectangular cross section (size approximately 2 x 2 x 35 mm<sup>3</sup>) with a diamond saw Brillant 200 (ATM GmbH, Mammelzen, Germany). Then the samples were thoroughly cleaned and dried over several days under vacuum prior to all experiments.

The influence of the polydopamine coating on the properties of the composite was studied by comparing the data with the data of a reference sample consisting of unfunctionalized TiO<sub>2</sub> particles granulated with poly(vinyl butyral) (PVB-TiO<sub>2</sub>). The unfunctionalized TiO<sub>2</sub> particles had a mean diameter of 200 nm, which is too small for granulation in the spouted bed apparatus. Therefore an alternative method for coating the particles through dispersion in a solvent was used. The solvent used in the process was ethanol. Approximately 200 g of TiO<sub>2</sub> particles were dispersed in 400 mL ethanol with the use of ultrasonic bath for approximately 1 h. A 6 wt% solution was prepared by dissolving 34.5 g poly(vinyl butyral) in ethanol with rigid stirring. Then the solution was mixed together with the TiO<sub>2</sub> particle dispersion. After 1 h rigid stirring and sonication a rotational evaporator was used in order to remove the solvent. After drying, the PVB-TiO<sub>2</sub> agglomerates were milled to an agglomerate size between 40 and 500 μm and subsequently hot-pressed at the same conditions as described above. The sample preparation for the mechanical testing was carried out in the same way compared to the composites with polydopamine functionalized TiO<sub>2</sub> particles. In both composites with and without polydopamine the weight fraction of polymer was approximately 15 wt%, leading to a ceramic fraction of 85 wt% as it is discussed in the thermal analysis part below.

## **2.4 Characterization methods**

### **2.4.1 Infrared spectroscopy**

Fourier transform infrared spectroscopy (FT-IR) was carried out with a Bruker Alpha FT-IR spectrometer (Bruker GmbH, Germany) in the attenuated total reflectance mode (ATR), equipped with an ATR-diamond crystal, in a spectral range of 400 - 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 64 scans. The different materials were placed directly on the ATR-diamond crystal. In order to perform the experiment a small amount of the sample was grounded in an agate mortar with an agate pestle.

### **2.4.2 Thermogravimetric analysis**

Thermogravimetric analysis (TGA) was performed using a TG 209 F1 Iris (Netzsch, Selb, Germany). The experiments were done in a temperature range from 25 °C up to 900 °C at a heating rate of 10 K/min. The measurements were performed under argon atmosphere.



Approximately 10 mg of the grounded material was placed in a ceramic pan for the measurements.

#### 2.4.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) experiments were carried out using a calorimeter DSC 1 (Mettler-Toledo, Gießen, Germany), within a temperature range from room temperature to 250 °C. The heating rate used was 10 K/min. Three heating-cooling cycles were accomplished since the first heating interval served for erasing the sample thermal history. In most cases the second heating interval was used for the evaluation of the thermal properties except from the case of the PVB-TiO<sub>2</sub>@PDA that the additional third heating-cooling cycle was evaluated as well. The measurements were performed under nitrogen atmosphere. Approximately 10 mg of the polymer and of the grounded composites were placed in an aluminum pan of 10 µL after drying over several days under vacuum.

#### 2.4.4 Morphological characterization

The morphology of the particles and the composites were examined by scanning electron microscopy using a Zeiss Supra VP55, at an accelerating voltage of 1 kV (Carl Zeiss AG, Jena, Germany) equipped with a secondary electron SE2 detector. A small amount of the powder of the TiO<sub>2</sub> particles (with and without coating) or a small amount of the compression-molded composites, respectively, was placed on a metal pin sample holder and stabilized with carbon tape. For the investigation of the composites after nanoindentation experiments, the specimens were prepared *via* freeze fracture under nitrogen. Non-sputtered samples were examined in order to investigate the structure's appearance.

#### 2.4.5 Rheology

Experiments in the torsion mode were performed using a rotational rheometer MCR 502 (Anton Paar GmbH, Graz, Austria) in a nitrogen atmosphere with the solid rectangular fixture tool SRF12. The frequency  $f$  was 1 Hz. Before the experiments, a strain sweep at 25 °C in the interval of 0.02% – 0.2% was carried out in order to determine the linear viscoelastic range. For the temperature sweep experiment, the strain amplitude was set to 0.05%. The temperature range in this test mode was 25 to 150 °C and the heating rate 1 K/min. The time for temperature equilibration after insertion of the sample into the rheometer was 20 min. The gap distance of the clamp holders was chosen according to the dimension of the rectangular shaped samples.

#### 2.4.6 Mechanical characterization

Mechanical properties of the fabricated composite materials were studied *via* nanoindentation tests. These experiments were carried out with the Agilent Nano Indenter G200 system (Agilent Technologies, Waldbronn, Germany) using the CSM (continues stiffness measurement) option with a constant strain target of  $0.05 \text{ s}^{-1}$ . The maximum indentation depth was set to  $2 \mu\text{m}$ . The system was equipped with a Berkovich tip. For the nanoindentation tests the sample surface had to be smooth. Therefore the prepared rectangular samples were polished with diamond suspensions on a polishing machine (Saphir 350 equipped with head Rubin 520, ATM GmbH, Mammelzen, Germany). The surface roughness of the sample was reduced down to  $1 \mu\text{m}$ .

#### 2.4.7 Gel permeation chromatography

Gel permeation chromatography (GPC) measurements were performed at  $50 \text{ }^\circ\text{C}$  using dimethylacetamide as eluent solvent on a Waters instrument (Waters GmbH, Eschborn, Germany), equipped with polystyrene gel columns of  $10$ ,  $10^2$ ,  $10^3$ ,  $10^4$  and  $10^5 \text{ \AA}$  pore sizes, using a refractive index (RI) detector. Polystyrene standards of different molecular weights were used for the calibration of the instrumentation.

#### 2.4.8 Particles size distribution

For the estimation of the size of the polymer coating on the particles, the particle size analyzers Zetasizer Nano ZS (Malvern, Worcestershire, UK) and Camsizer XT (Retsch Technology GmbH, Haan, Germany) were used for analysis of small, submicron-sized,  $\text{TiO}_2$ -particles and the large, micron-sized, particle clusters, respectively. For the experiments on the Zetasizer, due to the small size of the particles a suspension was prepared in water (Millipore,  $0.055 \mu\text{S/cm}$ ) while in the Camsizer XT the particles were measured as prepared in gravity dispersion mode.

### 3 Results and Discussion

#### 3.1 FT-IR Spectroscopy

The ATR-FT-IR spectra of pristine and polydopamine coated  $\text{TiO}_2$  particles as well as pristine poly(vinyl butyral) and the composite of poly(vinyl butyral) with the polydopamine coated  $\text{TiO}_2$  particles are presented in Figure 2. In comparison to the pure  $\text{TiO}_2$  particles, the characteristic vibrations of the polydopamine coating are visible at wavenumbers of

approximately  $1500\text{ cm}^{-1}$ ,  $1290\text{ cm}^{-1}$ , and  $1070\text{ cm}^{-1}$  attributed to C-O, C=O and C-N bond vibrations, respectively. [34] The characteristic vibrations of poly(vinyl butyral) are observed at  $1750\text{ cm}^{-1}$  and in the range from approximately  $1450\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$ , attributed to the vibrations from carbonyl groups as well as to the C-H, C-C and C-O vibrations of the structure, respectively. [35] At high wavenumbers (approximately  $3500\text{ cm}^{-1}$ ) the characteristic stretching vibrations from the hydroxyl groups are slightly observed. In case of the final hierarchical composite the characteristic vibrations of polydopamine and poly(vinyl butyral) are slightly observed as indicated by the three different boxes in Figure 2. The characteristic vibration of  $\text{TiO}_2$  is dominant and apart from that there is also an increase of absorption which is explained by the different sample preparation and the strong water uptake of polydopamine as well as by the hydrophilicity of the poly(vinyl butyral). The signals of the polydopamine coating are visible regardless of the additional poly(vinyl butyral) coating due to the low polymer amount. This is possible due to the large excess of the ceramic content in the composite and also to the grounding of the samples.

With respect to the interaction of the polydopamine coating with poly(vinyl butyral), the differences between the spectra are very small. A significant broadening is observed in the interval of  $2800 - 3600\text{ cm}^{-1}$ . In this range the characteristic stretching vibrations from the free O-H groups are to be expected, similar to what is visible also in case of poly(vinyl butyral), as it contains hydroxyl groups. Additionally, in the same wavenumber range of the spectrum of the composite a shift of the positions of the small peaks to lower wavenumbers is only hardly visible. These observations could be indications of hydrogen bond formation as in case of hydrogen bonding through the hydroxyl groups, the characteristic stretching vibration on the O-H bond is significantly affected and becomes more broad, see [36, 37].

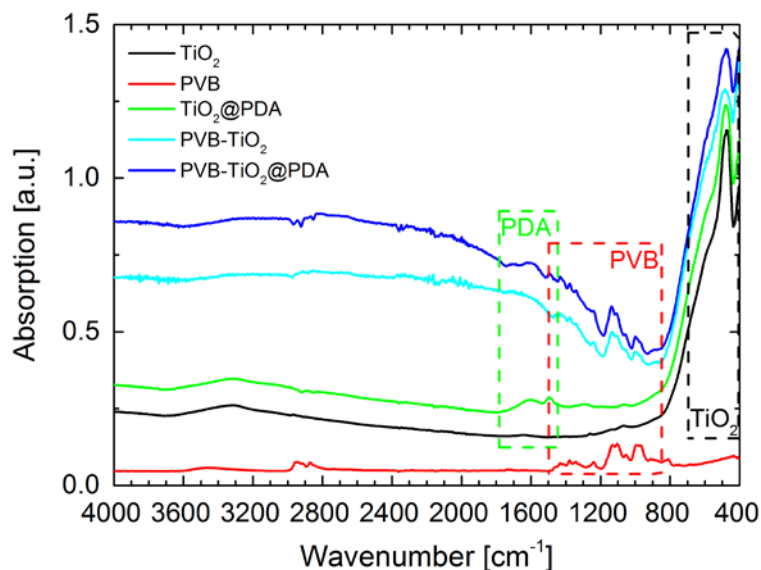


Figure 2. ATR-FT-IR spectra of the pure  $\text{TiO}_2$  particles, the pure PVB, the  $\text{TiO}_2$ @PDA particles as well as the PVB- $\text{TiO}_2$  and the PVB- $\text{TiO}_2$ @PDA composites. The spectra are shifted vertically for clarity.

### 3.2 Thermal Analysis

The DSC experiments provide important information about the thermal properties of the materials. In Figure 3 the results based on the second heating interval are presented. Only in case of the PVB- $\text{TiO}_2$ @PDA the third heating was also used. The pure  $\text{TiO}_2$  particles and the particles coated with polydopamine exhibit a constant heat flow as a function of temperature, indicating that the sample undergoes no thermal transitions. The pure poly(vinyl butyral) polymer shows a glass transition temperature at 69 °C, in agreement with literature. [11] The glass transition temperature of poly(vinyl butyral) for the composite PVB- $\text{TiO}_2$  is observed at 64 °C. In case of the composite PVB- $\text{TiO}_2$ @PDA the thermograph is very significant. In the second heating interval (PVB- $\text{TiO}_2$ @PDA(1)) there are two thermal transitions observed at 70 °C and at 85 °C, respectively. The first transition corresponds to the glass transition of poly(vinyl butyral) while the second transition could be attributed to the interaction of the polydopamine coating with poly(vinyl butyral) coating that hinders the transition of the poly(vinyl butyral) chains. It is known from literature that polydopamine contains hydroxyl and amine functional groups. Poly(vinyl butyral) contains 18 – 21 wt% OH groups according to the producer. Therefore the possibility of hydrogen bonding between poly(vinyl butyral) and polydopamine is high. Nevertheless, it is expected that the increase of the temperature affects the formation of hydrogen bonding. [37, 38] This is the reason for the

additional heating step of the DSC experiment. As it is observed in the DSC thermograph of the third heating interval (PVB-TiO<sub>2</sub>@PDA(2)), only one thermal transition at 67 °C is found, corresponding to the glass transition of poly(vinyl butyral). The second transition is not observed anymore, indicating that the hydrogen bonds were affected after heating.

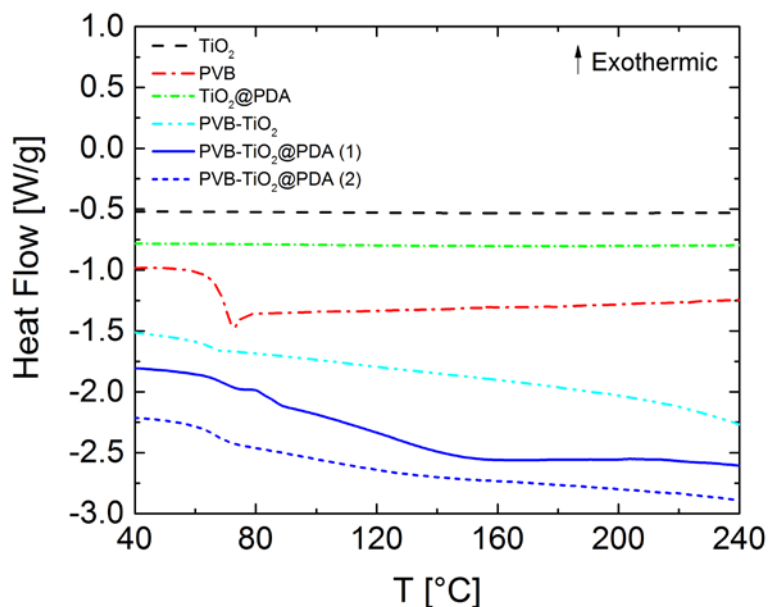
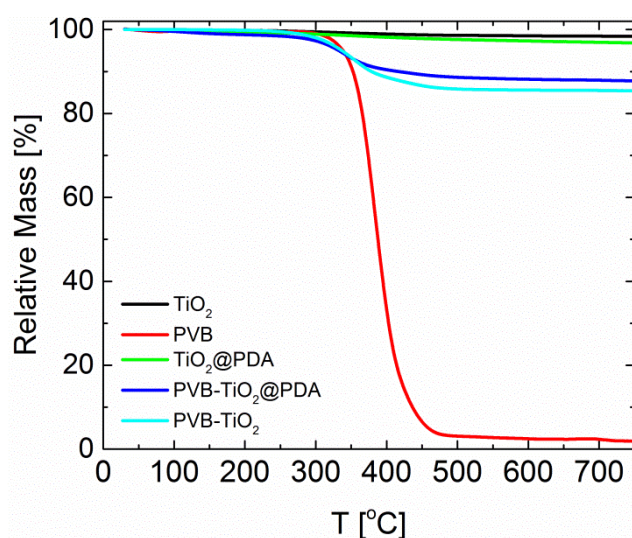


Figure 3. DSC thermographs of the pure TiO<sub>2</sub> particles, the pure PVB, the TiO<sub>2</sub>@PDA particles, the PVB-TiO<sub>2</sub> and the PVB-TiO<sub>2</sub>@PDA composites. The experiment was carried out under nitrogen atmosphere with a heating rate of 10 K/min. The curves are vertically shifted for clarity.

In Figure 4(a), the thermographs of the pure TiO<sub>2</sub> particles, the TiO<sub>2</sub> particles coated with polydopamine, the pure poly(vinyl butyral), and the two different types of composites are shown. The thermogravimetric analysis reveals that the TiO<sub>2</sub> particles were functionalized with approximately 2 - 3 wt% polydopamine. Polydopamine exhibits a complex decomposition and considering that the functionalization with polydopamine leads to formation of a very thin layer on top of the particles only an approximation of the weight fraction can be given through thermogravimetric analysis. In case of the final composites the total weight fraction of the organic phase was approximately 15 wt% in both cases. The samples indicated a high thermal stability up to 350 °C. Additionally, the thermal stability of the composites was investigated by the derivative of the relative mass as a function of temperature. As it is observed in Figure 4(b), for the pure and the polydopamine functionalized TiO<sub>2</sub> particles no minima in the derivative exist. Nevertheless for the pure poly(vinyl butyral) as well as for the composites PVB-TiO<sub>2</sub> and PVB-TiO<sub>2</sub>@PDA some differences in the minima of the derivative of the relative mass appear. The pure PVB shows a

minimum of the derivative of the mass loss at 383.5 °C while for the composites the temperature of the minima is significantly lower. The minimum of the derivative for the composite PVB-TiO<sub>2</sub> is observed at 354.0 °C and for the PVB-TiO<sub>2</sub>@PDA at 336.0 °C. The decrease of the minimum of the derivative of the mass loss can be attributed to the fact that the particles with the polydopamine coating enhance the decomposition of the polymer. The effect is even more pronounced in case of the polydopamine coated TiO<sub>2</sub> particles due to the hydrogen bonds that are also affected accelerating the degradation.

(a)



(b)

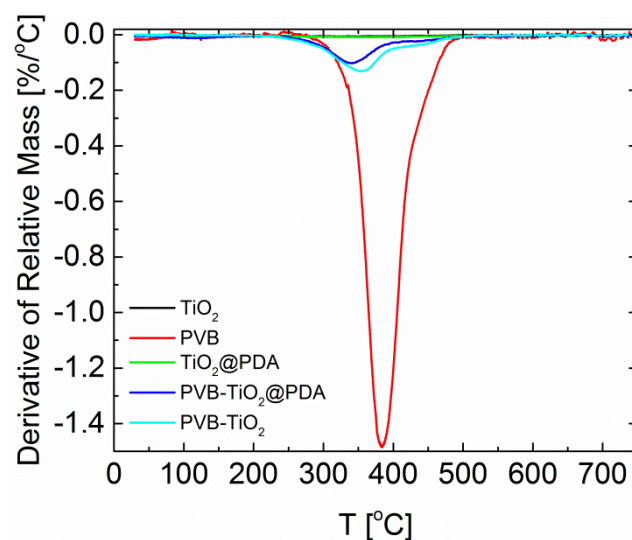


Figure 4. (a) Relative mass and (b) derivative of relative mass as a function of the temperature of the pure TiO<sub>2</sub> particles, the pure PVB polymer, TiO<sub>2</sub>@PDA particles, the PVB-TiO<sub>2</sub> and the PVB-TiO<sub>2</sub>@PDA composites. The heating rate was 10 K/min. The measurements were performed under argon atmosphere.

### 3.3 Structural and Size Characterization of the Particles and the Composites

The SEM micrographs of the particles are shown in Figure 5. In Figure 5(a), the pristine  $\text{TiO}_2$  particles are shown. The particles exhibit a rutile structure and are not significantly agglomerated. The mean particle diameter is approximately 200 nm. After coating with polydopamine the particles appear connected into larger blocks forming large agglomerates of about 100-500  $\mu\text{m}$ . As described above, the agglomerates were milled to a size of 20-40  $\mu\text{m}$  for the coating in the spouted bed. In Figure 5(b) the surface of the 20-40  $\mu\text{m}$  sized  $\text{TiO}_2$ @PDA agglomerates is shown. On the surface the small agglomerated particles are visible. This agglomeration was beneficial and enabled after milling the coating *via* the spouted bed technique. In Figure 5(c) it is observed that the agglomeration of the particles was more pronounced leading to coarser particle clusters. They were also milled to a size of 40-500  $\mu\text{m}$ .

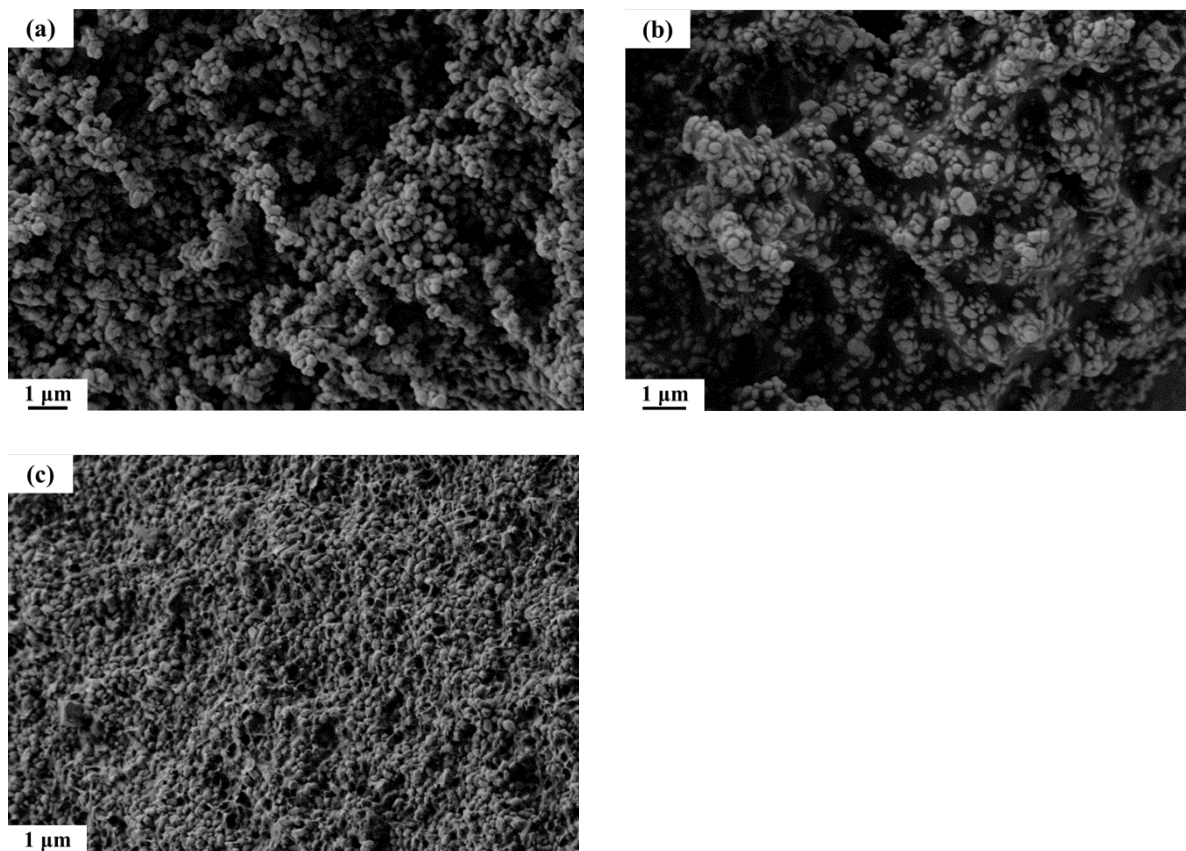


Figure 5. Scanning electron micrographs of (a) pristine  $\text{TiO}_2$  particles, (b)  $\text{TiO}_2$ @PDA-granules ( $\text{TiO}_2$  particles coated with polydopamine) and (c) PVB- $\text{TiO}_2$ -agglomerates (the composite of PVB with  $\text{TiO}_2$  particles without polydopamine coating).

The structure of the PVB-TiO<sub>2</sub>@PDA composites is presented in Figure 6(a). In this case the particles are agglomerated with a cluster size of 40 - 200 μm. These particles were used for the rheological and mechanical tests. In Figure 6(b) a fractured specimen similar to that used for the rheological and mechanical tests is shown. Although the particles are closely packed, cracks are visible which result from the material preparation. The organic coating on the surface of the particles influences the particle interactions, while the cracks influence the properties of the composites at the macro-scale.

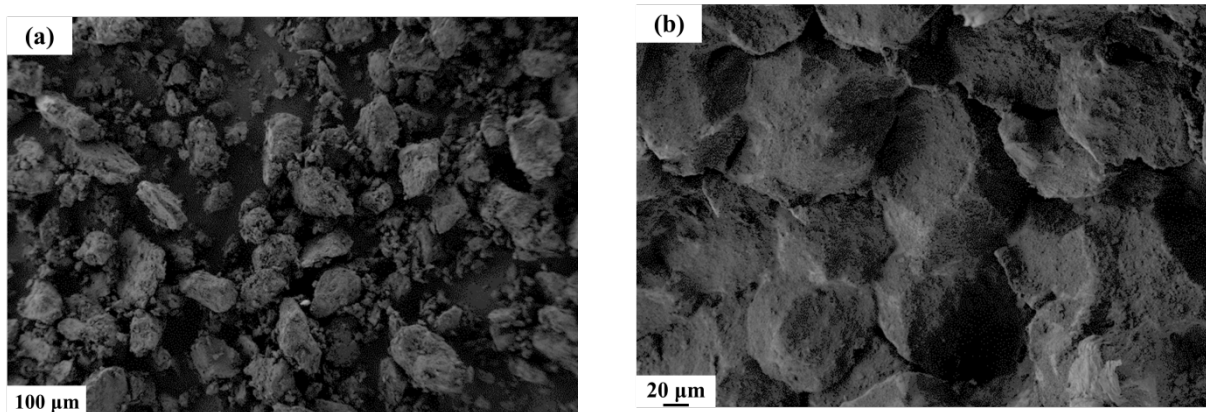


Figure 6. Scanning electron micrographs of (a) the PVB-TiO<sub>2</sub>@PDA agglomerates and (b) the fractured PVB-TiO<sub>2</sub>@PDA composite used for the nanoindentation experiments.

Due to the fact that the SEM micrographs are done without metal sputtering (e.g. platinum) the charging effect is very high and it is very difficult to estimate the size of the particles' coating. However, for the estimation of the polymer coating on particles, the particle size distribution of TiO<sub>2</sub>-submicroparticles is measured with a Zetasizer Nano ZS. The determined median diameter of particles  $d_{50}$  is about 195 nm. With this diameter and mass fraction of PDA which is approximately 3%, the coating layer of PDA can be estimated to approximately 3.5 nm. As already mentioned above TiO<sub>2</sub>-particles agglomerate after coating with PDA and agglomerates of 20-40 μm are then coated in the spouted bed with PVB. Correlating the mean size of agglomerates which is found with Camsizer XT to be approximately 30 μm and the mass fraction of PVB which is approximately 12%, the coating layer thickness of PVB on agglomerates can be estimated at 2.2 μm.

### 3.4 Rheology

The results of the dynamic-mechanical thermal analysis are presented in Figure 7. The storage modulus  $G'$  and loss modulus  $G''$  are plotted as a function of temperature  $T$ . At lower



temperatures the moduli of the ceramic composites are higher than the moduli of the polymer. Comparing the storage modulus of the composite based on the non-coated particles with the data of the composite based on the polydopamine coated particles it is observed that the composite with the non-coated particles attains a larger value. The glass transition temperature of the PVB polymer is identified by the maximum of the loss modulus at approximately 67.5 °C which is in close agreement with the DSC value. Above this temperature the values of the dynamic moduli decrease. Comparing the two different composites it is observed that the maximum of the loss modulus  $G''$  is shifted by approximately 15 °C. This is a strong indication of the influence of the polydopamine coating on the composite. Remarkable is that at higher temperatures the storage and the loss moduli do not lead to a cross-over which indicates that a network of the ceramic fillers dominates the mechanical response. Additionally, at elevated temperatures the dynamic moduli for the composite with the polydopamine coated particles attain higher values than the composites with the uncoated particles meaning that the filler-filler interactions are even stronger in the presence of polydopamine. The viscoelastic properties of highly filled composites are strongly influenced by filler-filler, polymer-filler and polymer-polymer interaction. [11] Our data reveal that the filler-filler interactions are very important. Nevertheless the polymer-filler interaction in case of the polydopamine coated particles significantly contributes to the measured moduli.

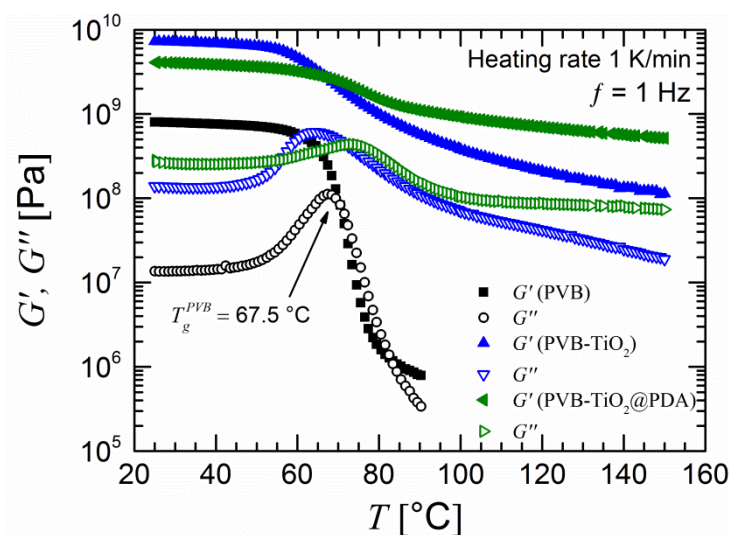


Figure 7. Temperature dependence of the dynamic moduli  $G'$  and  $G''$  obtained by dynamic-mechanical thermal analysis of pristine PVB, the PVB/TiO<sub>2</sub> and the PVB/TiO<sub>2</sub>@PDA composites.

### 3.5 Micromechanical Analysis

In order to examine the intrinsic mechanical properties of the two different composites, the Young's modulus and the hardness were determined by nanoindentation experiments. The results of these investigations are presented in Figure 8.

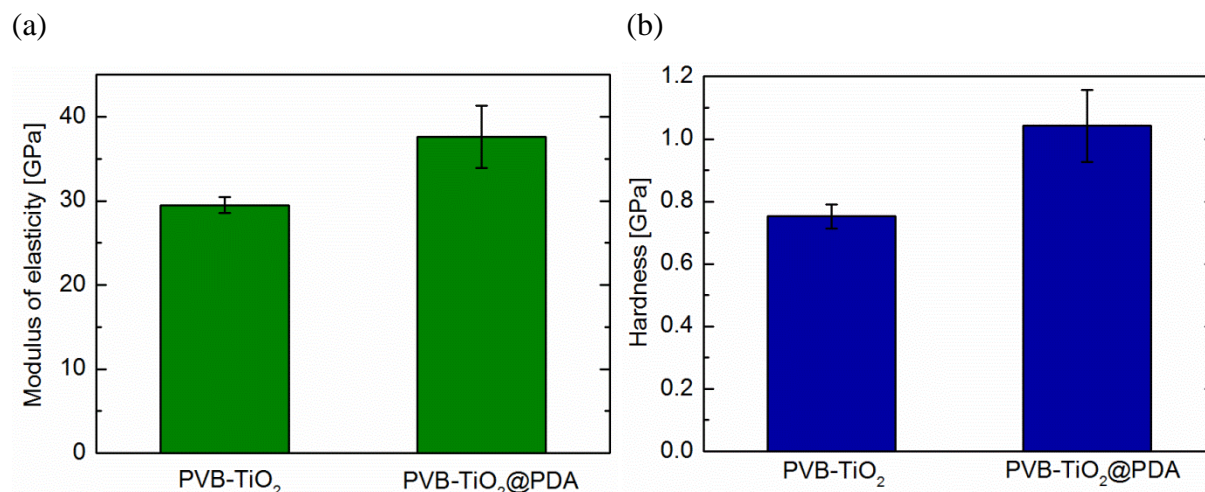


Figure 8. (a) Modulus of elasticity and (b) hardness of PVB-TiO<sub>2</sub> and PVB-TiO<sub>2</sub>@PDA composites measured by nanoindentation.

The results of the nanoindentation tests demonstrate a significant increase of the mechanical properties in composites in which TiO<sub>2</sub> particles were first functionalized with polydopamine in comparison to composites without the polydopamine coating. The modulus of elasticity increased from 29.5±1.0 GPa for the composites with uncoated TiO<sub>2</sub> particles to 37.7±3.7 GPa for the composites with TiO<sub>2</sub>-particles that were coated with polydopamine. These values correspond to an increase of approximately 27% for the modulus of elasticity for the composite with polydopamine coated TiO<sub>2</sub> particles. Hardness exhibits an even higher increase of approximately 38% related to the hardness of the composite with the unfunctionalized TiO<sub>2</sub> particles, i.e. an increase from 0.75±0.04 GPa to 1.04±0.12 GPa for the composites with uncoated and coated with polydopamine TiO<sub>2</sub> particles, respectively.

### 3.6 Concept on the Structure of the Composites

Our experimental analysis leads to the concept that a weak interaction appears between the polydopamine coating and the poly(vinyl butyral) coating in this composite. The concept is presented in Figure 9 and derives from the process of the hierarchical composite fabrication with the polydopamine as the first hierarchical level and the poly(vinyl butyral) the second hierarchical level. In Figure 9, the TiO<sub>2</sub> particles are coated with polydopamine (black color) through adhesion of the polydopamine *via* the amine groups. Poly(vinyl butyral)

(cyan color) surrounds the particles and interacts with the polydopamine hydroxyl functional groups leading to the formation of hydrogen bonds. This hydrogen bonding has a positive influence on the mechanical properties of the composites as already discussed above. Nevertheless, this effect is a reversible process since the sample is not chemically crosslinked. The hydrogen bonding is a weak type of bonding that affects the composite properties modifying reversibly the polymer properties.

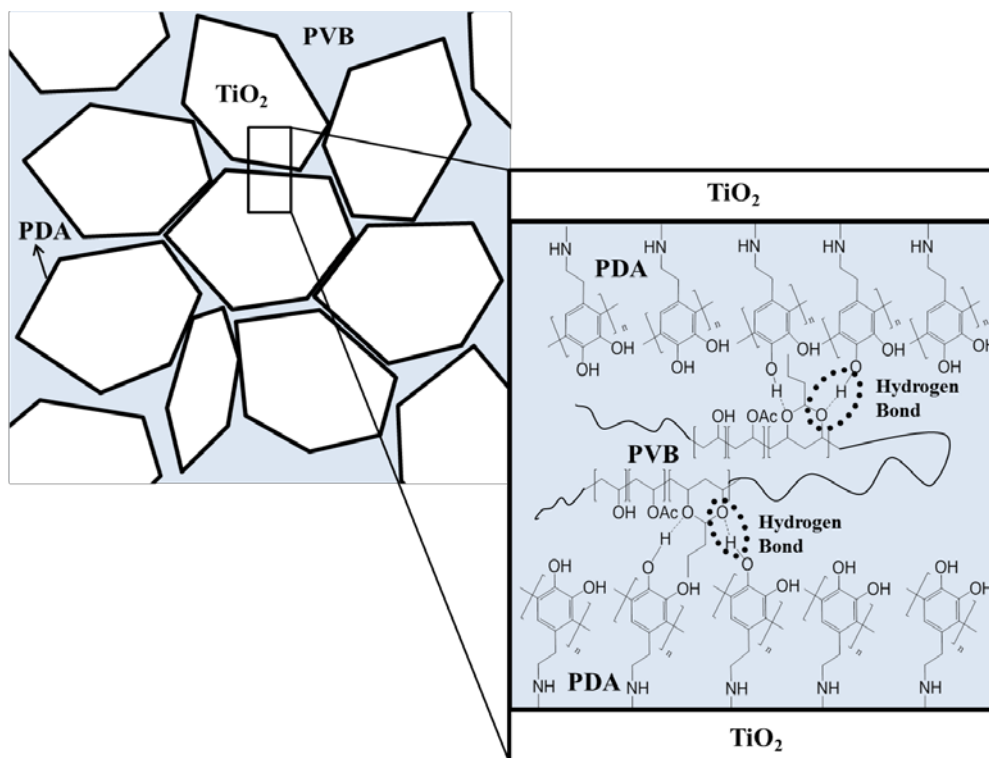


Figure 9. Schematic representation of the morphology of the PVB-TiO<sub>2</sub>@PDA composites. The hydrogen bond is a result of the interaction of the poly(vinyl butyral) and the polydopamine coating of the particles and is illustrated in the interface between two particles. The hydrogen donor drawn in the scheme is the O-H group of the polydopamine monomeric unit and the acceptor is the oxygen from the poly(vinyl butyral) monomeric unit.

Support for this approach is given by gel permeation chromatography data with focus on poly(vinyl butyral). Pristine PVB as well as extracted PVB from the composite were measured. PVB was extracted from the composite with ultra-sonication at 50 °C from a dimethylacetamide solution. The sample was left to rest after the ultra-sonication and the particles precipitated. The supernatant of the solution (containing the dissolved PVB) was filtered in order to be sure that only pure polymer solution was injected into the instrumentation. Most of the PVB can be extracted from the composite but due to the high filling degree and also the fact that the particles will draw away some of the polymer it is

assumed that some not extracted PVB remains there. The number average molecular weight ( $\bar{M}_n$ ), the weight average molecular weight ( $\bar{M}_w$ ), the peak molecular weight ( $\bar{M}_p$ ) and the polydispersity index ( $\mathcal{D}_M$ ) of the pristine and extracted poly(vinyl butyral) are summarized in Table 1 below. The number and the weight average molecular weight of the pristine and the extracted poly(vinyl butyral) indicated a small increase for the case of the extracted polymer as well as decrease of the polydispersity of the polymer. These minor changes can be interpreted as insignificant since the sample has a broad molecular weight distribution. What is important to be mentioned is that there is no observation of secondary peaks at higher molecular weights and that PVB was possible to be extracted from the composite without indication of polymer gel formation. This is a strong evidence of non-chemical crosslinking since in the opposite way the polymer would be inseparable from the composite. Therefore, as it was expected hydrogen bonding had a minor impact on the polymer properties and not a permanent effect as in cases of chemical crosslinking.

Table 1: Molecular characteristics of poly(vinyl butyral) from GPC experiments. The molecular weight is listed in g/mol.

Poly(vinyl butyral)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_p$	$\mathcal{D}_M$
Pristine	37 200	87 600	71 600	2.4
Extracted	57 800	95 000	70 800	1.6

The rheological analysis shows that the addition of the particles increases the dynamic moduli of the pristine polymer which is in agreement with data for highly filled alumina/PVB composites [11]. In case of highly filled composites not only the interaction of the particles with polymer, but also the particle-particle interactions significantly contribute to the dynamic moduli. It is important to note that the composites of PVB with polydopamine coated TiO<sub>2</sub>-particles exhibit at room temperature slightly lower storage modulus, while at temperature above the glass transition temperature of PVB the inverse phenomena is observed. This is an additional indication of the interaction between the PVB and the PDA coating; nevertheless the results could not be directly compared with the results of the mechanical analysis based on the nanoindentation measurements. The explanation behind this is that in the first case the measurement is done on a macroscopic scale (sample dimensions of 2 x 2 x 25 mm<sup>3</sup>), while in nanoindentation the mechanical properties are only locally estimated in a very small area (nano-scale vs micro-scale). In addition, since the rheological measurements were performed in the torsion mode (shear deformation), the factor 2(1+ $\nu$ ) (Poisson ratio  $\nu$ ) which is in the

range between 2 and 3 for a comparison with the tensile modulus obtained by nanoindentation has to be taken into account.

#### **4 Conclusions**

In this work, the influence of a polydopamine coating in composites of TiO<sub>2</sub> with poly(vinyl butyral) was studied. An FT-IR spectroscopy analysis demonstrated the successful coating of the TiO<sub>2</sub> particles with polydopamine. The thermal analysis revealed that the particles were coated with approximately 3 wt% polydopamine. The interactions of the functionalized particles with poly(vinyl butyral) were studied in detail by thermal analysis, scanning electron microscopy, rheological experiments and micromechanical analysis. The thermal stability of the composites is decreased due to the interaction of polydopamine with poly(vinyl butyral), i.e. the hydrogen bonding is affected as a result of the heating. The scanning electron micrographs show that the polydopamine coating leads to the agglomeration of the particles and the successful use of the spouted bed technique. The polydopamine coating also influences the dynamic moduli of the composite in comparison to pristine poly(vinyl butyral). More specifically the addition of the particles leads to a significant increase of the dynamic moduli in case of the composites, which is reversible after heating at high temperatures. From the mechanical analysis the composites with the use of non-coated TiO<sub>2</sub> particles exhibit a hardness of  $0.75 \pm 0.04$  GPa and a Young's modulus of  $29.5 \pm 1.0$  GPa. On the other hand, the composites with the use of polydopamine coated TiO<sub>2</sub> particles are associated with an increase of hardness of approximately 38% and an increase of Young's modulus of approximately 27% in comparison to the composites with uncoated TiO<sub>2</sub> particles. In summary, the formation of hydrogen bonds between the polydopamine coating and the poly(vinyl butyral) led to composites with high mechanical stability at room temperature.

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