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CH-π Interactions as the Driving Force for Silicone-Based Nanocomposites with Exceptional Properties**

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Among the various issues pertaining to the use of composite polymeric materials based on nanoparticles, the dispersion of the nanofillers in the matrix and the nature of the filler-polymer interface are central. In many cases, poor dispersion results in agglomeration or phase separation, leading to a dramatic loss of the materials properties. To overcome this problem, a number of strategies have been developed with various degrees of success. They usually come at a high price, due to the necessity of modifying the surface state of the filler. Here, we report on novel carbon nanotubes-reinforced poly(dimethyl)siloxane nanocomposites and surprisingly, for which the use of "self pure" multiwall carbon nanotubes, i.e., without any surface functionalization or specific surface treatment, turns out to be the most efficient approach to impart new key-properties to the silicone matrix. Viscometric, rheological and theoretical studies have been performed that demonstrate the remarkable potential of dispersing a very tiny amount of "self pure" carbon nanotubes in silicone, paving the way to unexpected applications, e.g., in the field of fire endurance. Very interestingly, only tiny amounts of MWCNTs are required: usually less than 0.5 wt %. Those properties all rely on the nature of the nanotube-silicone interface interactions, which are dominated by additive CH-π interactions between the methyl groups of the polymer and the nanotube surface.

Polydimethylsiloxane (PDMS) is the most common silicone elastomer owing to its ease of fabrication and advantageous chemical/physical properties, such as low surface energy, low glass transition temperature and high chain mobility.[1] Currently, to compensate for their poor mechanical properties, silicone materials have to be reinforced by incorporation of particulate materials, silica being the most commonly used filler. To date, the *in situ* filling process, where silica is generated into the elastomeric matrix, is the most efficient way to fill PDMS materials.[2] However, this reinforcement still requires a relatively high mass fraction of minerals (> 10 wt %). Over the past few years, much attention has been paid to polymer nanocomposites, which represent a rational alternative to conventional filled polymers, especially polymer-layered silicate nanocomposites.[3,4] In spite of their many potential applications, only a few reports have been published on polydimethylsiloxane nanocomposites.[5–8] The key-point for the improvement of properties as diverse as the mechanical, the thermal, and the barrier performances is the effective/individual dispersion of the nanofillers in the matrix. To reach this objective, the type of nanofillers, their size and the nature of the interface formed within the matrix all have to be optimized. In this context, carbon nanotubes (CNTs) are of prime interest; however, they have a strong tendency to agglomerate in densely packed bundles, and their dispersion in polymers still remains a major challenge.

Here we discuss first the spectacular change in the physical and rheological behavior of the PDMS resin when a very low amount (0.5 wt %) of "self-pure" carbon nanotubes (MWCNTs) is added into the silicone matrix. Figure 1a–d is extracted from a video available as Supporting Information on line information (Movie S1).[9]

Classically, the unfilled PDMS is a very fluid liquid, Figure 1a. Upon adding 0.5 wt % MWCNTs to the unfilled matrix (Fig. 1b) and a mechanical blending, a huge increase in viscosity is observed, which results in a PDMS matrix that has totally lost its capacity to flow (Fig. 1c). Quite interestingly, MWCNTs also act as rheo-thinning agents, allowing for the first time brush-paint (poorly filled) PDMS with a very low

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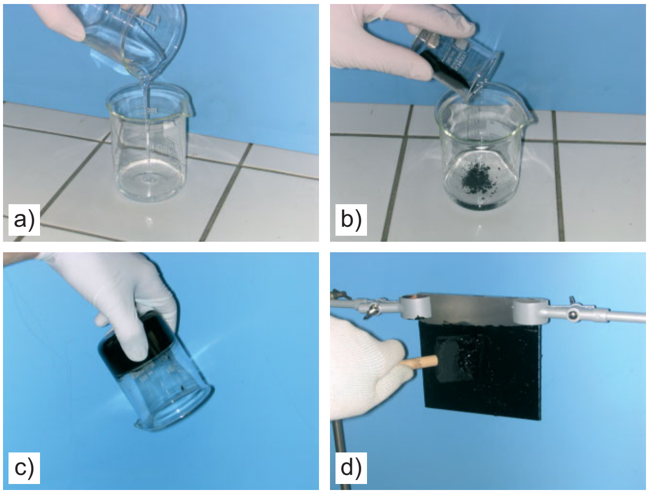

Figure 1. A) Unfilled PDMS is a fluid resin; B) A tiny amount (0.5 wt %) of MWCNTs is added to the matrix; C) After mechanical blending, PDMS is no longer flowing; D) CNTs act as rheothinning agents allowing brush-paint PDMS application, even at such low content.

filler content, prior to the cross-linking reaction (Fig. 1d), for any orientation of the substrate. Since the capacity of a polymer fluid to flow has a direct correlation with the dispersion and the orientation of nanofillers in the matrix,[10] the viscosity of the blends has been measured as a function of the filler content. For the sake of comparison, PDMS filled with surface-treated carbon nanotubes (TMWCNTs), or a needle-like magnesio-silicate nanofiller (natural sepiolite clay), or a commercially available organo-modified layered alumino-silicate clay (Montmorillonite from Southern Clay Products, Texas: Cloisite 30B®) were also prepared and analyzed. The treatment of the carbon nanotubes consists in a multi-step process (basic and acid treatments) leading to a partial oxidation of the nanotube surface. From the measurements, a viscosity value of 4980 cP can be extracted for the neat matrix. Significant differences are found between the three types of nanofillers (Fig. 2). A very slight increase in viscosity is observed as the Cloisite 30B® content is increased. However the values remain very low and do not exceed 5900 cP for a solid fraction as high as 5 wt %. In the case of the natural sepiolite filled PDMS, the increase of viscosity is more pronounced than for Cloisite 30B®, with values reaching 7940 cP for 5 wt % loading. The most spectacular effect is observed with the untreated carbon nanotubes: the viscosity values strongly increase between 0.1 wt % (+ 25 %), and 0.3 wt % (+ 280 %), for which a value of 14000 cP is reached. A clear illustration of the importance of the surface state of the filler is provided by the lower viscosity observed when the carbon nanotubes are treated, with values below 7000 cP at a filler content of 0.5 wt %.

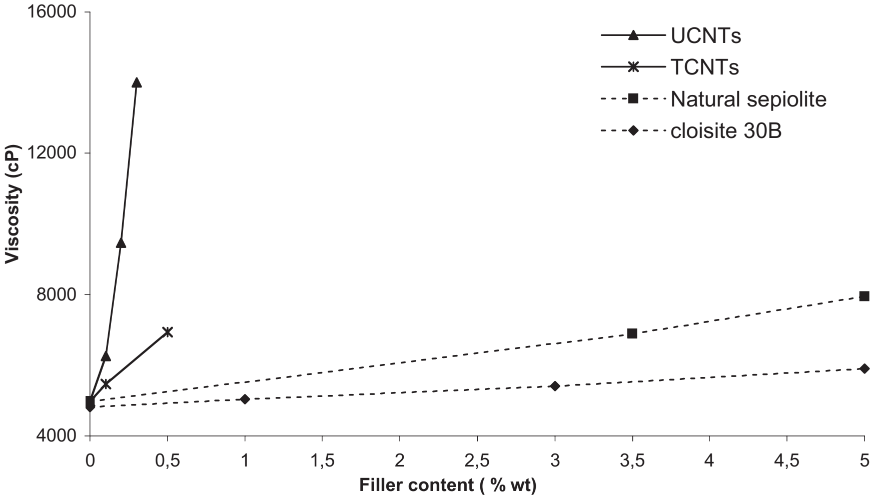

Figure 2. Influence of the nature filler on the viscosity of the PDMS resin.

The rheological behavior of PDMS filled with "self-pure" carbon nanotubes has been studied in more details by following the viscosity against the shear rate. The results are shown in Figure 3 for two nanofiller contents (0.5 and 0.7 wt %). For the unfilled system, the viscosity is independent of the shear rate over a broad range (5–200 s^{-1}). On the contrary, the filled systems exhibit two different regimes. As long as the shear rate is low (< 40–50 s^{-1}), the viscosity decreases with increasing shear rate; then, for higher shear rate values, the viscosity reaches a constant, minimum value. Clearly, the nanofilled silicon behaves as a thinning fluid.

The strength or density of filler-polymer interactions can be correlated to the amount of PDMS chains adsorbed per gram of CNTs after a solvent extraction (Q_{ads}). This quantity is determined via "bound rubber" tests (see methods). Only PDMS composites filled with natural sepiolite or untreated carbon nanotubes show a significant amount of adsorbed polymer at the nanofillers surface after extraction. As is the case in the viscosity study, the more pronounced effects are observed with the carbon nanotubes as fillers. For example 2.5 g of polymer per gram of nanofiller are adsorbed when natural sepiolite is the filler while the value increases to more than 20 g per gram of nanofiller with MWCNTs as fillers. These experiments and observations allow classifying the PDMS blends, according to the nature of the filler: (i) minor effects are detected when the organomodified montmorillonite is used as clay reinforcement of the PDMS matrix. This observation is not surprising, since this filler has no particular affinity toward the silicon matrix, as recently described by Schmidt et al.[11] (ii) the use of natural sepiolite seems to be a rather efficient route to reinforce the polymer matrix. The increase of viscosity at relatively low mass fraction (<10 wt %) can be seen as a first sign of favorable polymer-fillers interactions, as confirmed by the "bound rubber" tests. These

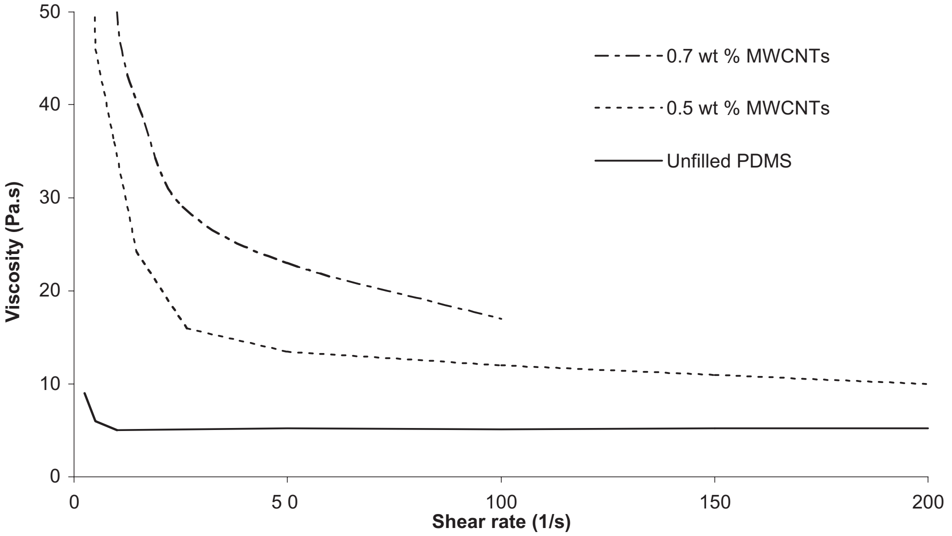

Figure 3. Evolution of the viscosity vs. shear rate.

results are quantitatively close to those observed with silica particles, which currently are the filler of choice to reinforce silicon elastomers.[12] Favorable interactions between the OH groups, due to the presence of silanol functions along the natural sepiolite surface, and PDMS backbone have been reported in the literature.[13] (iii) among all studied nanofillers, the “self pure” carbon nanotubes investigated here provide unprecedented improvement in the properties of silicone elastomer nanocomposites, even for extremely low filler content (< 0.5 wt %).

Since the nature of PDMS-CNT interactions is fundamental for the efficiency of the filler in reinforcing the polymer matrix, modeling studies (based on molecular dynamics (MD) simulations) were performed to assess at the microscopic level the adsorption properties of PDMS on the surface of carbon nanotubes. The simulations were carried out on a model system consisting in an armchair single-wall carbon nanotube ($N = M = 6$) that interacts with a single PDMS chain (ranging in size from 12 to 200 repeating units). As initial structures in the MD simulations, the polymer chains were built according to an elongated helical-like conformation[14] and brought in van-der-Waals contact to the nanotube. Figure 4A shows a typical structure obtained after a 400 ps simulation at 300 K in the NVT canonical ensemble (see also the animation available as Supporting Information on line information, Movie S2).[9] It can be clearly seen that the polymer chain completely wraps around the CNT surface. A detailed analysis of the atomic spatial distribution shows that the PDMS chains organize to form a regular radial pattern with, when moving away from the CNT surface: (i) a first layer of methyl groups pointing towards the CNT; (ii) the oxygen and silicon atoms belonging to the polymer backbone; and (iii) an outer layer formed by the remaining methyl groups, Figure 4B. The calculations show that about one methyl group out of two binds to the CNT surface (i.e., belongs to the first layer around the CNT). An adsorption energy per repeat unit converging to ~ (2.6 ± 0.1) kcal mol^{-1} in the longest chains can be extracted by averaging over the MD trajectories after equilibration. Such physical adsorption of the PDMS chains onto the CNT is mostly triggered by CH-p interactions[15] between the PDMS methyl groups and the π-electron-rich surface of the carbon nanotube. CH-π interactions are weak hydrogen bonds between soft acids and soft bases; they are largely due to dispersion forces and partly to charge-transfer and electrostatic forces. The calculated adsorption energy per repeating unit corresponds to roughly three times the typical value for a CH-π interaction (about 1.0 kcal mol^{-1}),[16] which is consistent with the picture above of one methyl group per repeating unit binding to the surface. It is worth stressing that the energy destabilization induced by the change in conformation upon going from the isolated PDMS chain to the chain wrapped around the CNT is minute (less than 0.6 kcal mol^{-1} per repeating unit), which, together with the presence of a high density of methyl groups amenable to CH-π bonding, explains the unique adsorption properties of PDMS on CNT surface. Based in this model, other ‘CH-rich’ polymers, such as polyethylene or polypropylene, would also be expected to interact strongly with the pure CNT surface? However, the lower chain flexibility of those compounds, compared to PDMS, and their higher ability to crystallize, reduce the density of the CH-π interactions per CNT surface area. Along the same line, the presence of polar groups and other chemical defects on the surface of the treated CNTs is expected to decrease the global strength of the CH-π interactions, which is consistent with the much lower performances of the TMWCNTs/PDMS blends.

These experimental and theoretical results not only provide invaluable insight into fundamental aspects related to the structural organization and energetics of CNT based nanocomposites, but also pave the way to new industrial and prac-

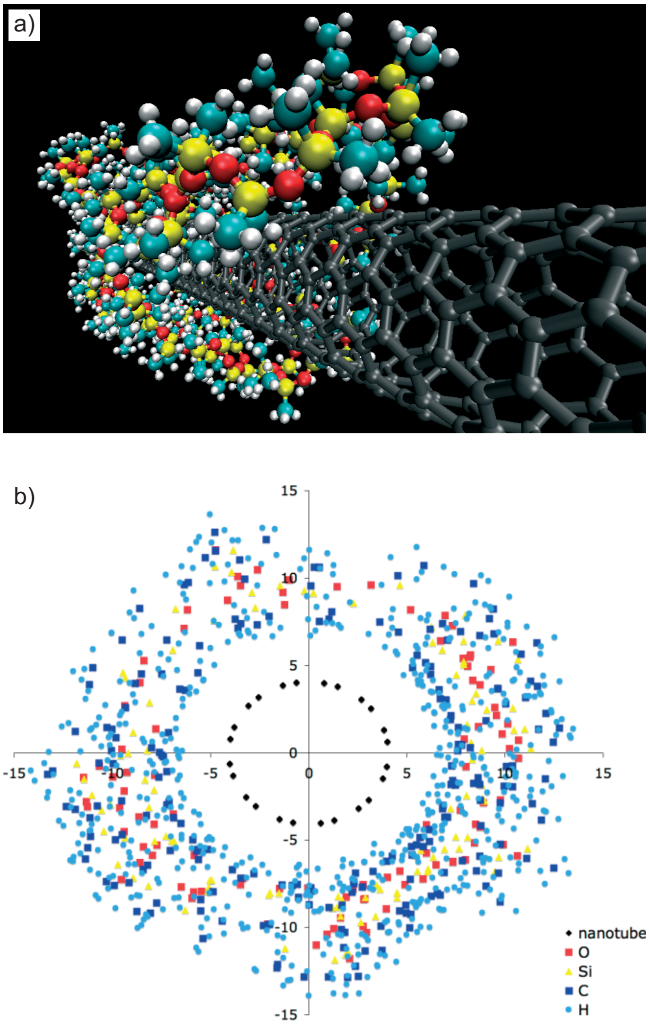

Figure 4. A) Final structure after a 400 ps MD run. The PDMS chain is completely wrapped around the carbon nanotube. B) Projection of the atomic coordinates on the plane perpendicular to the nanotube axis. Distances are in Å. (color code: H atoms in light blue; C atoms of PDMS in dark blue; C atoms of CNT in black; O atoms in red; Si atoms in yellow).

tical developments based on such silicone materials. These novel reinforced PDMS indeed exhibit a number of remarkable properties. As an example, we report here the fire endurance of aluminum plates coated with a PDMS layer containing a tiny amount of "self-pure" carbon nanotubes (Fig. 5). When exposed to a flame of 1050 °C (60 kW m^{-2}; see methods), the temperature of the unprotected plate increases to 380 °C within a few minutes, which causes the fast destruction of the plate. The fire endurance times (on the order of 80 min) of the plates coated with nanofilled PDMS are much longer compared to those coated with unfilled PDMS (around 15 min) and the maximum temperature reached in the presence of the nanofillers (290 °C) is much lower than the corresponding value for neat PDMS (405 °C). These results unambiguously demonstrate the significant improvement in fire resistance of substrates protected by MWCNT-filled silicone. This phenomenon can be attributed to the thermal percolation phenomenon where the number of thermal conductive paths increases with the nanofiller content and to a very high thermal conductivity of the carbon nanotubes well known in the literature.[17] Along the same line, the dispersion of the MWCNTs in the silicone matrix leads to the formation of an electrically percolated network. As a result, the resistivity of the system drops from 1.63×10^{14} Ω cm for the unfilled silicone down to 2×10^{4} Ω cm upon addition of the MWCNTs at a very modest loading of 0.2 wt %.

In conclusion, the use of "self pure" carbon nanotubes as nanofillers represents a most remarkable route to produce high performance silicone elastomer nanocomposites in terms of properties and applications. For instance, the exceptional rheological properties of these new systems make it possible to brush-paint a silicon fluid (before the cross-linking reaction) for any orientation of the substrate, even at extremely low mass fraction of carbon nanotubes (< 0.5 wt %). The improvement in the fire resistance properties and unexpected biological properties (not described here) are other examples of the wide range of applications that can be envisioned for these novel silicone composites.

Experimental

PDMS (Sylgard 184) was purchased from Dow Corning. This formulation contains two separate parts, which need to be mixed together to prepare cross-linked materials. For the viscometric and rheological studies, we have not cross-linked the material. We used only a α,ω-vinyl-terminated PDMS with a degree of polymerization equal to 434 and a partially cross-linked PDMS functionalized with terminal carbon double bonds. The "self pure" multiwall carbon nanotubes (MWCNTs, i.e., nanotubes that have never undergone any surface treatment after being produced by CCVD; Grade 7500) were kindly supplied by Nanocyl S.A; PDMS and fillers are mechanically blended with a helical blade at 1200 rpm for 2 h 30 min before characterization.

For "bound rubber" tests, each blend (typically 3.5 g; containing 0.05 wt % nanofillers) is introduced in a glass tube containing a magnetic stirring bar. Approximately 30 g of heptane are added to the blend, so that the PDMS concentration is the same in every experiment. The mixture is placed under stirring at a controlled temperature (25 °C) during 4 h. The tube is centrifuged (4000 rpm, 10 min), and the products (nanofiller + adsorbed PDMS) are dried under vacuum at 70 °C until mass stabilization. Then Q_{ads}, the mass of absorbed polymer per gram of nanofiller is calculated with Mf the dried mass after stabilization and X the weight ratio of nanofiller in the initial mixture.

$$Q_{ads} = \frac{Mf - [3.5 - (X/100) * 3.5]}{3.5 - (X/100) * 3.5}$$

The MD simulations were carried out with the free molecular package TINKER: http://dasher.wustl.edu/tinker, using the MM3 force field [18,19]; the image is rendered by VMD [20]; the total energy of the system is obtained by optimizing several points along the MD trajectory. Removing the CNT then yields the energy of the PDMS chain in the adsorbed conformation. The difference between these two energies is the adsorption energy.

The fire resistance of aluminum plates coated with cross-linked PDMS containing "self-pure" MWCNTs (thickness 4 mm) was tested.

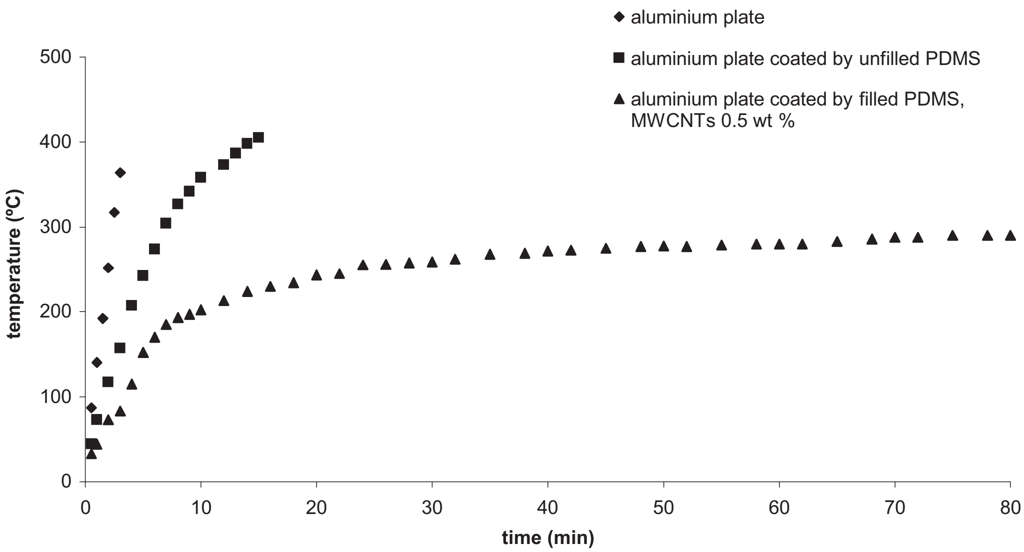

Figure 5. Fire endurance of aluminum plates protected with a PDMS coating.

The metal silicone adhesion was promoted with a functionalized silane coupling agent. The coated face was exposed to a flame (1050 °C; 60 kW m^{-2}) at a constant distance (3 cm). The temperature of the non coated face was measured at regular intervals via a thermocouple until the end of the test (destructuration of the aluminium plate or complete degradation of the coating).

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[1] W. A. LeE, R. A Rutherford, in *Polymer Handbook*, 2nd ed. (Eds: J. Brandup, E. H. Immergut), Wiley, New York **1975**.

[2] J. E. Mark, *Acc. Chem. Res.* **2006**, *39*, 881.

[3] M. Okamoto, S. S. Ray, *Prog. Polym. Sci.* **2003**, *28*, 1539.

[4] M. Alexandre, Ph. Dubois, *Mater. Sci. Eng.* **2000**, *R28*, 1.

[5] S. D. Burnside, E. P. Giannelis, *Chem. Mater.* **1995**, *7*, 1597.

[6] S. J. Wang, C. F. Long, X. Y. Wang, Q. Li, Z. Qi, *J. Appl. Polym. Sci.* **1998**, *69*, 1557.

[7] A. Beigbeder, S. Bruzaud, P. Mederic, T. Aubry, Y. Grohens, *Polymer* **2005**, *46*, 122279.

[8] T. Horsch, G. Serhatkulu, E. Gulari, R. M. Kannan, *Polymer* **2006**, *47*, 7485.

[9] https://mail.materianova.be/beigbeder/; login: beigbeder; password: movie-07.

[10] Y. Y. Huang, S. V. Ahir, E. M. Terentjev, *Phys. Rev. B* **2006**, *73*, 125422.

[11] D. F. Schmidt, F. Clement, E. P. Giannelis, *Adv. Funct. Mater.* **2005**, *16*, 417.

[12] R. Al Alkoum, *Ph.D. Thesis*, Université de Haute Alsace **2004**.

[13] L. Bokobza, *J. Appl. Polym. Sci.* **2003**, *93*, 2095.

[14] M. T. Khorasami, H. Mirzadeh, Z. Kermani, *Appl. Surf. Sci.* **2005**, *242*, 339.

[15] M. Nishio, M. Hirota, Y. Umezawa, *The CH/p Interaction: Evidence, Nature and Consequences*, Wiley-VCH, New York **1998**.

[16] K. Shibasaki, A. Fujii, N. Mikami, S. Tsuzuki, *J. Phys. Chem. A* **2006**, *110*, 4397.

[17] P. Kim, L. Shi, A. Majumdar, P. L. McEuen, *Phys. B* **2002**, *323*, 67.

[18] B. Y. Ma, J. H. Lii, N. L. Allinger, *J. Comput. Chem.* **2000**, *21*, 813.

[19] N. L. Allinger, Y. H. Yuh, J. H. Lii, *J. Am. Chem. Soc.* **1989**, *111*, 8551.

[20] W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics* **1996**, *14*, 33.