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Morphology of self-assembled polyvinyl alcohol/Silica nanocomposites studied with atomic force microscopy

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Summary

Atomic force microscopy (AFM) is used for the morphology study of polyvinyl alcohol/silica (PVA/SiO_2) nanocomposites prepared by incorporating solution compounding and self-assembly technique. The results show that the strong particle-particle interaction of SiO_2 nanoparticles is greatly suppressed, and the SiO_2 nanoparticles are homogenously distributed in PVA matrix as spheric nano-clusters. The average size of the SiO_2 nano-clusters is below 50 nm at low SiO_2 loadings (≤5 wt%). At higher SiO_2 contents, the particle aggregations can be clearly observed, and the average size of SiO_2 aggregates significantly reach up to 110 nm and 250 nm at SiO_2 content of 10 wt% and 15 wt%, respectively. AFM height profiles demonstrate that the surface heterogeneity of the nanocomposite is governed by the SiO_2 contents. The surface roughness evaluated as root mean square (RSM) of peak-to-valley height values shows that the surface becomes rougher as the SiO_2 content increases, particularly, a remarkable increase in surface roughness is found at the SiO_2 content of 10 wt%.

1. Introduction

The latest developments in nanotechnology provide a unique opportunity to create revolutionary polymeric/inorganic nanocomposites (PINs) with significant properties [1-3], which only occur when their morphologies are organised at nano-scale. Nanoparticles, the “designer molecules” govern the macroscopic behaviour PINs, in which the way the nanoparticles and polymer arranged in the composites is essential to determine the properties of the PINs. Therefore, the morphology of nanocomposites or distribution pattern of nanoparticles in polymer matrix is one of the most important criteria for successful creation of nanocomposites.

Atomic force microscopy (AFM) has become one of the most valuable tools for investigating the morphology of PINs [4, 5]. Among all microscopic techniques, AFM allows one to perform complex analysis of materials surfaces and near-surface regions at nanometer scale with a simple sample preparation. In particular, AFM provides information on surface roughness values at a high resolution level which presently cannot achieved by the other techniques [6].

In our previous works, a novel polyvinyl alcohol/silica (PVA/SiO_2) nanocomposite developed by incorporation of the solution compounding and self-assembly technique was presented. In comparison with the pure PVA, the resulting nanocomposite possesses significantly improved thermal resistance [7], mechanical properties [8], and different crystallisation behaviour [9, 10] is also observed. In the present paper, we employ AFM to investigate the effect of SiO_2 on the morphology and surface roughness of the PVA/SiO_2 nanocomposites. The microstructure of the SiO_2 nanocluster in PVA matrix is also observed.

2. Experiments

2.1. Materials

All experimental materials were supplied by Sigmar-Aldrich (Sigma-Aldrich, Louis, MO.), and used as received. The average molecular weight of polyvinyl alcohol (PVA) (product No. 81383) is 67,000, degree of hydrolysis and polymerisation is 86.7-88.7 mol% and 1400, respectively. The average molecular weight of polyallylamine hydrochloride (PAH) (product No. 28,322-3) is 70,000. The fumed SiO_2 nanoparticles (product No. S5505) have an average diameter of 14 nm and surface area of 200 ± 25 m^2/g.

2.2. Nanocomposite preparation

The nanocomposites were prepared according to the method described in our earlier works [7-10]. Firstly, the SiO_2 nanoparticles are negatively charged and act as templates to adsorb positively charged PAH molecular chains through electrostatic adsorptive interaction. PVA molecular chains are then assembled on the surface of SiO_2 nano-particles via hydrogen bonding interaction between hydroxy groups of PVA and amino groups of PAH. Finally, the treated SiO_2 nanoparticles are uniformly dispersed in bulk PVA matrix. The resulting nanocomposites are named by abbreviations based on their content of nanoparticles. For example, N-5 represents the nanocomposite with the SiO_2 content of 5 wt%.

2.3. Charaterisation methods

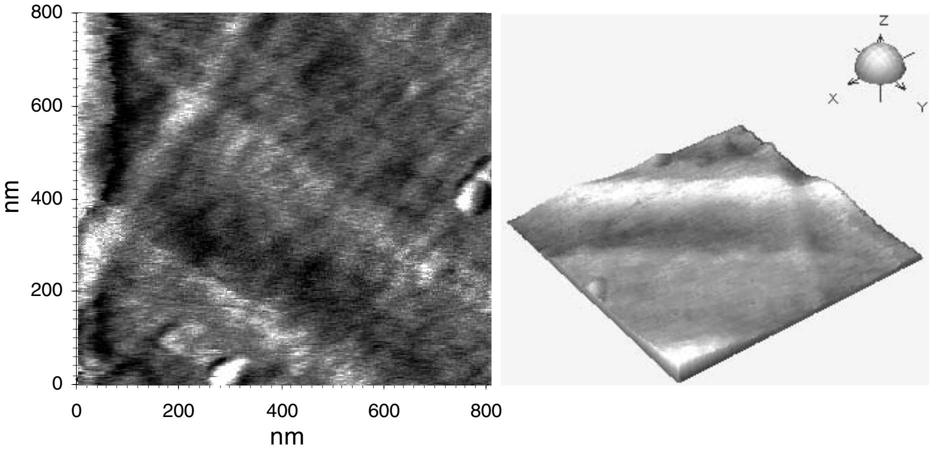
The surface for AFM measurement was obtained by filming the nanocomposite dispersions on the mica wafers. AFM measurement was made on a Nano-III Digital Instrument (Nihon Veeco KK, Tokyo, Japan) with a tapping mode. Prior to AFM observation, the film surface was checked by an optical microscopy to ensure a continuous and flat surface without any breakage or damage.

Thin film for transmission electron microscopy (TEM) (JEM-100CXII instrument, JEOL, Peabody, MA) observation was prepared by dropping the nanocomposite dispersion on a copper grid coated with a carbon film. The accelerating voltage is 100 keV.

3. Results and discussion

3.1. Distribution of SiO_2 nanoparticles in PVA matrix

The topograph and 3-dimensional image of the PVA/SiO_2 nanocomposite with a SiO_2 loading of 0.5 wt% (N-0.5) are shown in Fig. 1. The SiO_2 particles hardly appear in these graphs, as the SiO_2 loading is too low. However, some rough areas can be clearly observed in the surface because of the introduction of SiO_2. When inorganic particles present in polymer matrixes, at the constant tapping oscillation amplitude (constant tapping force), the tip has to travel longer distance to reach the valleys between the primary particles. To maintain the constant force or constant separation distance between the tip and the surface, the tapping frequency will be delayed. The result of this delay is observed as the lower phase shift on the images. As a result, the contract in the valleys and the primary particles will appear to be different contrast from the smooth surface [11].

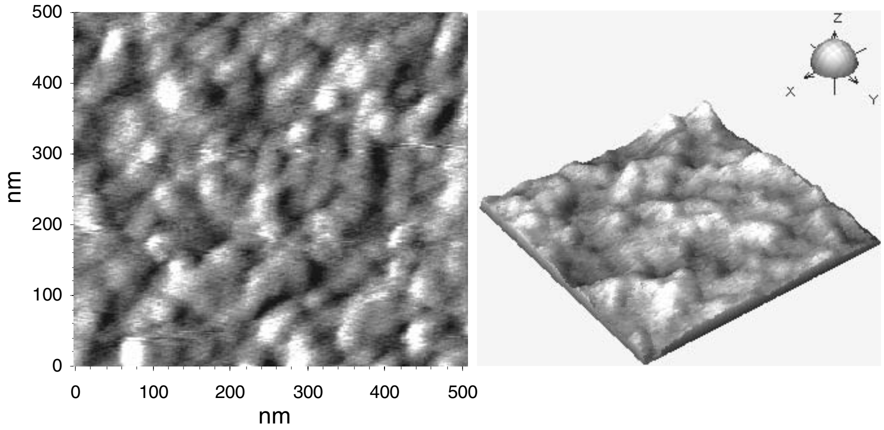


a) Topograph b) 3-D graph

Figure 1. AFM graphs of N-0.5

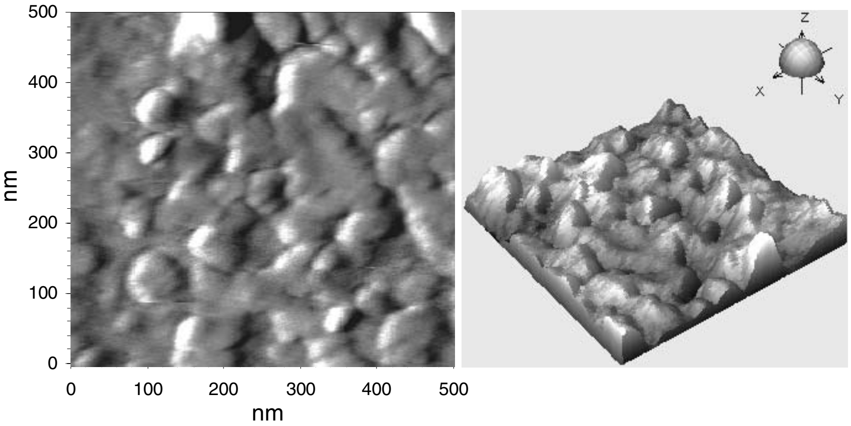
When 2 wt% SiO_2 is added into PVA, the SiO_2 particles can be clearly observed in PVA matrix (Fig. 2), where the valleys and edges of the SiO_2 particles appear darker and the surface of the SiO_2 appears brighter. The surface of the sample becomes rougher, as many undulations between valleys and peaks are presented. Many hemispherical particles can be observed in the 3-dimensional graph. These SiO_2 particles show a uniform size with a narrow distribution between 20 and 50 nm. Fig. 3 is the AFM graphs of N-5 nanocomposite. The size of the SiO_2 cluster is very uniform, and the average size is around 40 nm. From the 3-dimensional graph, it can be seen that the roughness of the surface is more obvious compared to N-2 and N-0.5, but still stands on the order of tens of nanometers.

Fumed silica nanoparticles have been extensively used to prepare polymer/silica nanocomposites via melt compounding [12] and other physical blending [13]. However, silica has a number of hydroxyl groups on the surface, which results in the strong filler–filler or particle-particle interactions and adsorption of polar materials by



a) Topograph b) 3-D graph

Figure 2. AFM graphs of N-2



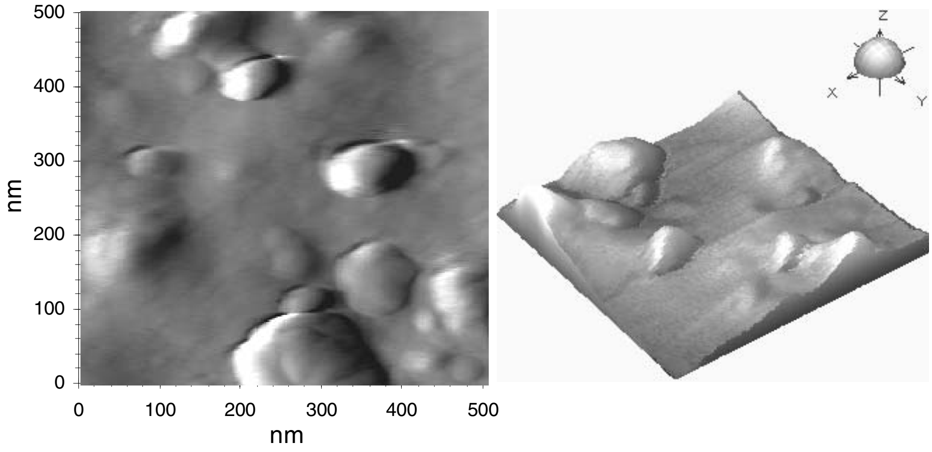
a) Topograph b) 3-D graph

Figure 3. AFM graphs of N-5

hydrogen bonding. SiO_2, therefore, has strong self-aggregation nature. In such conditions, the fumed SiO_2 nanoparticles trend to form loosely agglomerates that are dispersed with an average size in the range 300 ~ 400 nm, and these aggregated particles cannot be broken down by the shear forces during melt compounding [12].

Fortunately, the strong self-aggregation of SiO_2 nanoparticles, in the present work, has been greatly restricted, as illustrated by the above AFM graphs that the average size of the SiO_2 primary aggregations in the nanocomposite with SiO_2 content up to 5 wt% is successfully controlled at a level below 50 nm. This enables us to develop a PVA/SiO_2 nanocomposite with significant properties, while the melt compounding is not suitable for preparation of high performance nanocomposite, due to the aforementioned high aggregation of SiO_2 [14]. The remarkable restriction on the SiO_2 self-aggregation, in this work, attributes to the self-assembling treatment of SiO_2 nanoparticles. After the two steps of assembly, the SiO_2 particles are completely encapsulated by the PAH and PVA layers, which shield and interdict the strong particle-particle interaction of SiO_2 particles. Thus, the formation of SiO_2 aggregations is greatly suppressed.

However, a significant change of morphology is observed, when the SiO_2 loading reaches 10 wt% (Fig. 4). The size distribution of the SiO_2 cluster markedly increases to 20~300 nm, and 110 nm accounts for the majority. To investigate the macroscopical morphology of the SiO_2 cluster in N-10, the aggregation region is extensively observed with a lower resolution (Fig. 5). Although most of the SiO_2 clusters are homogenously dispersed in PVA matrix, quite a few secondary aggregations emerge in some regions where the mixing is not appropriately done.



a) Topograph b) 3-D graph

Figure 4. AFM graphs of N-10

Even if SiO_2 trends to further aggregate, the surface of the SiO_2 cluster, particularly at the edge of the cluster, is very smooth, no micro disfigurements at the interface of two phases can be clearly observed, implying the clusters still strongly interact with the PVA. This confirms our previous results observed with SEM [7, 9], i.e. after the self-assembly treatment, no phase separation is generated at SiO_2 loading up to 10 wt%.

As the SiO_2 loading increases to 15 wt%, the primary aggregations trend to form secondary aggregations, and many bulk aggregations with the size ranged from 300 nm to 1000 nm are found in PVA matrix (the average size is 250 nm statistically obtained from several AFM images) (Figs. 6 and 7). The roughness of the surface also significantly increases as observed from the 3-dimensional graph. From Fig. 7, it is clear that the interface between the SiO_2 aggregations and PVA is crude, and SiO_2 is

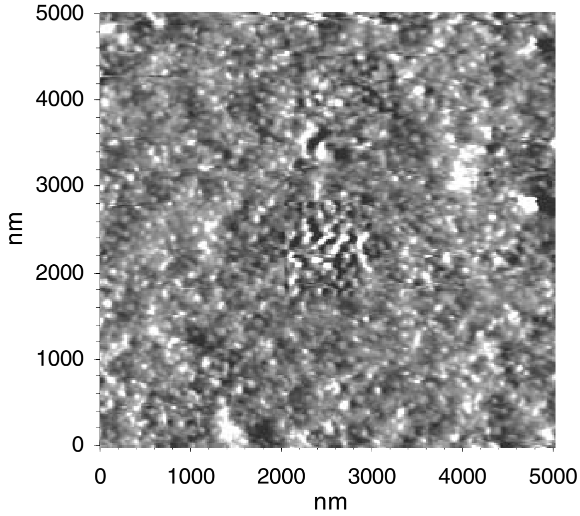
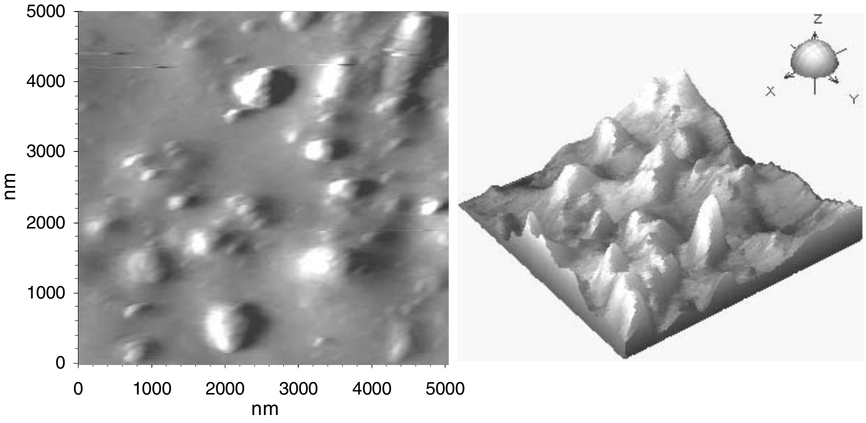


Figure 5. AFM topograph of N-10 (lower magnification)



a) Topograph b) 3-D graph

Figure 6. AFM graphs of N-15

not perfectly packaged by PVA due to the phase separation. Different from other samples, the random conformation of the SiO_2 agglomerates and some micro voids, deformations and microcracks are found in N-15. Although self-assembly treatment has greatly improved the dispersion of SiO_2 in PVA matrix, the aggregation becomes heavier with the increase of SiO_2 loading. In particular, at the SiO_2 content of 15 wt%, because of the overload, the SiO_2 shows a strong aggregation tendency.

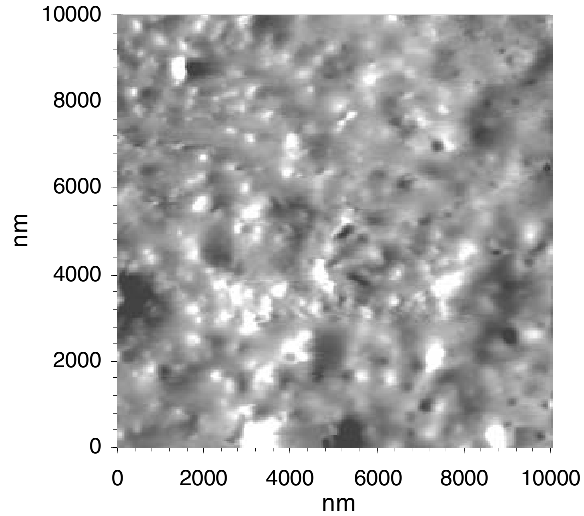


Figure 7. AFM topograph of N-15 (lower magnification)

3.2 Structure of SiO_2 nano-clusters

As the average size of original SiO_2 nanoparticles employed in this study is just 14 nm, SiO_2 particles that exceed this size are actually presented as nano-clusters comprising of several individual SiO_2 nanoparticles. These primary aggregations unlikely result from the particle-particle interaction, as the SiO_2 particles are completely encapsulated by the PAH and PVA layers after two steps of assembly. Thus, these aggregations are caused by the absorption between polymer molecular chain and SiO_2 nanoparticles, i.e. PAH and PVA molecular chains may adsorb quite a few individual nanoparticles to form nano-clusters. Similar assumption was found in polyethylene oxide (PEO)/silica nanocomposites [15, 16]. It was found that the molecular weight or the molecular length of PEO plays an extremely important role in the SiO_2 slight aggregation, as PEO with different molecular weight could interact or cover different amount of SiO_2 primary nanoparticles.

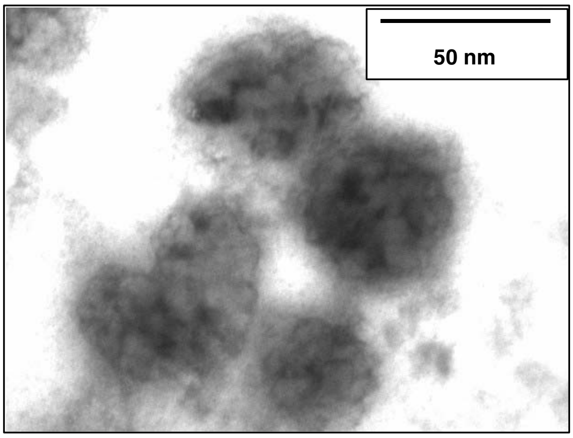
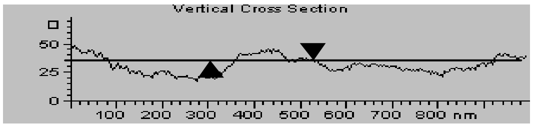


Figure 8. TEM micrograph of SiO_2 nano-cluster in PVA matrix

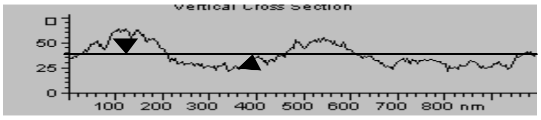
Interestingly, the SiO_2 clusters mainly appear a spherical structure as observed in Fig. 4, where the SiO_2 clusters is presented a hemispherical shapes as another half is encapsulated by the PVA. Some individual SiO_2 nanoparticles can even be seen in the clusters, although there is little significant difference in the phase contract. Another illustrative evidence is given by the TEM micrograph, where the spherical nano-clusters with diameter around 30 ~ 50 nm (presented as dark circle pies) are uniformly distributed in PVA matrix (Fig. 8). This confirms the proposed structure of SiO_2 cluster in our previous works [7, 9].

3.3 Surface roughness of the PVA/SiO_2 nanocomposite

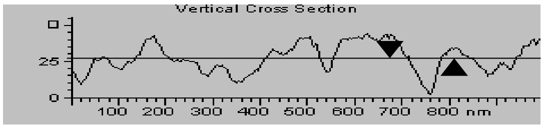
The fornamed 3 dimensional graphs provide only the optical impression of surface roughness of the PVA/SiO_2 nanocomposites. The AFM height profiles can offer a more objectively investigation of the roughness of the sample's surface (Fig. 9). The



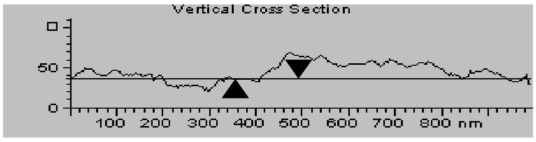
a) PVA



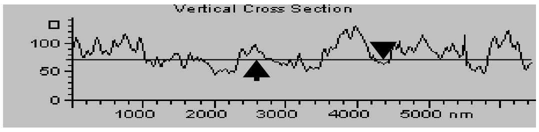
b) N-0.5



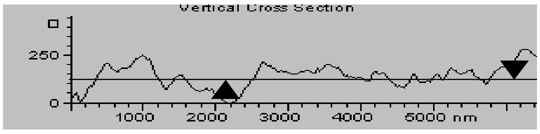
c) N-2



d) N - 5



e) N-10



f) N-15

Figure 9. Height profiles of PVA and nanocomposites

surface roughness can be presented as the height value of Z axes of the image, where the peak-to-valley height can be employed to assess the roughness. As a base for calculating the local roughness, artefact-free areas are chosen to obtain realistic values. The evaluation software of AFM provides an option to calculate the local roughness within any selected area on the surface.

The maximum peak-to-valley height of the pure PVA is about 25 nm (Fig.9a), indicating that the surface of the pure PVA is very smooth. As the loading of SiO_2 increases, the roughness gradually grows. When 5 wt% SiO_2 is added, the maximum peak-to-valley height of the sample increases to 60 nm (Fig. 9d), which still stays at the same level as the former samples. This fact implies that at low SiO_2 contents, the effect of SiO_2 content on the surface roughness is unimportant. However, the morphology of the surface changes significantly with further addition of SiO_2 (more than 10 wt%). Particularly, at the SiO_2 content of 15 wt%, the maximum peak-to-valley height reaches 280 nm (Fig. 9f).

To obtain more accurate surface roughness analysis, the average surface roughness can be assessed with root mean square (RMS) of peak-to-valley heights, which is calculated according to the following equation [6, 17]:

$$RMS = \sqrt{\frac{\sum_i^N (H_i - H_{ave})^2}{N}} \qquad \textbf{(1)}$$

where N is the number of measurement of height, Hi is a peak-to-valley height value, Have - an average peak-to-valley height within a given area. RMS is presented as a function of SiO_2 contents in Fig.10. As expected, RMS shows a strong dependence on the content of SiO_2. The samples with low SiO_2 contents are relatively smooth while those with higher SiO_2 contents show greater roughness and development of random

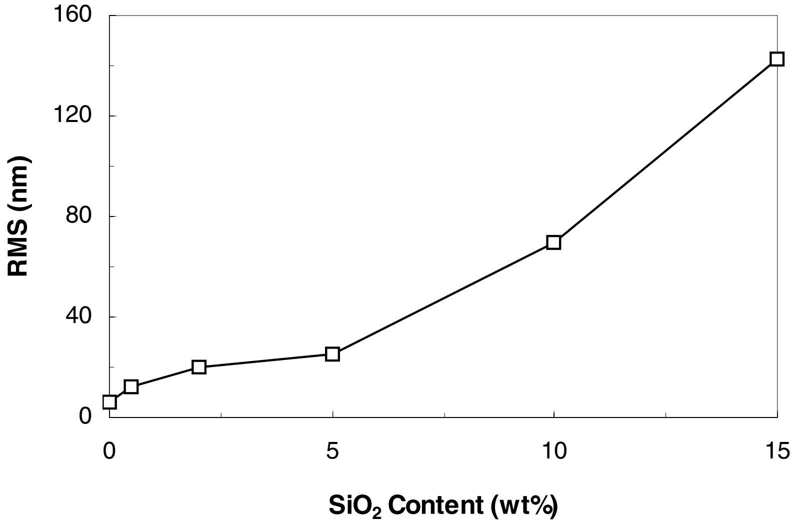


Figure 10. Dependence of RMS on SiO_2 content

agglomerates. The tuning point of this dependency is at the SiO_2 content of 10 wt%. Taking the previous data of the size distribution of the SiO_2 clusters into account, it is reasonable that a significant correlation exists between RMS and the size distribution of SiO_2 clusters.

4. Conclusions

The investigation of PVA/SiO_2 nanocomposite by AFM demonstrates that the self-aggregation of fumed SiO_2 caused by filler-filler interaction is greatly restricted by the self-assembly treatment. When only 5 wt% or less SiO_2 is added into PVA, the primary aggregation occurs to form spherical nano-clusters with an average size from 20 to 40 nm. With further addition of SiO_2 (10 wt% and 15 wt%), the secondary agglomerates based on the primary aggregation are formed as bulk aggregations with an average size of 110 nm and 250 nm, respectively. An excellent miscibility between SiO_2 and PVA is found in the nanocomposites with a SiO_2 loading up to 10 wt%.

The surface roughness of the nanocomposites described as root mean square (RMS) of average surface roughness shows a similar trend to the average size of SiO_2. The samples with low SiO_2 contents ($\leq$5 wt%) have a very smooth surface, whose RMS ranges from 6 nm to 25 nm. While at SiO_2 content of 10 wt% and 15 wt%, RMS increases significantly to 70 nm and 140 nm, respectively.

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