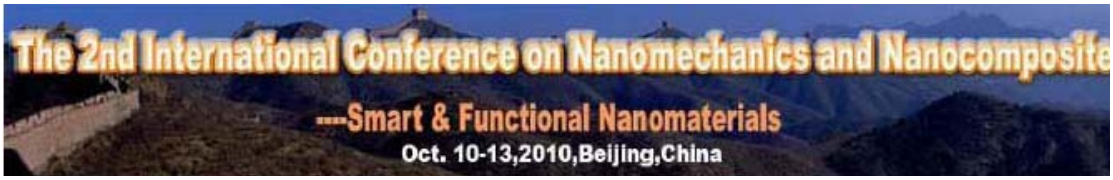

Dr. S. M. Zebarjad
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Aug 10, 2010

Dear Dr. Zebarjad,
We are pleased to inform you that your paper entitled “Effect of nano size TiO2 on morphology of polyurethane nanocomposite” (ID: H-004) has accepted for the forthcoming The 2nd International conference on nanomechanics and nanocomposites to be held in Beijing, China between 10th and 13th Oct 2010.
This letter serves as a formal invitation for you to attend the Symposium and give a poster presentation, which you may wish to use for visa application and funding purposes. We thank you for your contributions and support to this event, which we will strive to make it a fruitful and successful forum.

If you have any further quires, please do not hesitate to contact us.
Look forward to meeting you in Beijing in Oct.

Best regards,

Certification

To whom it may concern

It is to certify that Dr. S. M. Zebarjad has presented his paper entitled with "Effect of nano size TiO2 on Morphology of Polyurethane/TiO2 nanocomposites" to the 2nd International Conference on Nanomechanics and Nanocomposites which is held in Beijing, China during Oct. 10-13, 2010.

Sincerely yours,

Prof. Shaoyun Fu

Chairman of the 2nd ICNN

10/11/2010

Effect of nano size TiO_2 on morphology of Polyurethane/TiO_2 nanocomposites

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ABSTRACT: In the current research different content of nano-size TiO_2 powders were added into semi rigid polyurethane foam. Nano particles were dispersed into the polyol component by stirring and then heating during ultrasonication to avoid particle agglomeration. Both scanning electron and transmission optical microscopes were used to elucidate the role of nano-size TiO_2 on evolution of porous structure of polyurethane foam. Cell size distributions were obtained by measuring average cell diameters of existing cells in micrographs. To have a better assessment of nanoparticle effects on foam morphology, sample densities were measured using Archimedes law. The results showed that by increasing nanoparticle content, respectively an approximate decrease of 40% and 90% in cell size and density was achieved. Heat releasing rate and bubble formation depends strongly on Isocyanate/Polyol ratio as well as nanoparticles content.

KEY WORDS: Nano TiO_2 particles, Nanocomposite, Apparent density, Cell size, foam morphology

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KEYWORDS: Nano TiO_2 particles, Nanocomposite, PU foam, Cell size,

INTRODUCTION

Foam microstructure including cell size, cell wall thickness and foam density has a prominent role on physical and mechanical response of PU foams. In some researches, relation between some microstructural parameters on mechanical properties were modeled and investigated [1, 2]. Saint-Michel *et al.* [3] studied the effect of density on mechanical properties of high density PU foams. They succeeded in modeling the yield strength by assuming that foam density controls the microstructure.

Owing to the fact that specific area of nanoparticles is very high, they are prone to be attracted to each other by intermolecular van der Waals forces. This attraction causes clusters of agglomerated particles which play as defect in the composite. In order to avoid agglomeration, a focused external energy like ultra sound wave is applied to separate the particles in one of the liquid constituents of neat PU foam. One of the most prominent mechanisms of particle separation is acoustic cavitation. By this mechanism tiny bubbles are successively generated, grow and collapse which result into production of transient micro hot spots. These local areas with high temperature and pressure are favorable sites to overcome the attracting forces between particles and promote the wettability between nanoparticles and liquid polymer.

Nano TiO_2 particles are inclined to be attracted by OH groups of polyol, therefore nanoparticle dispersion into polyol with the aid of ultrasonication would be more efficient. By ascertaining a relation between microstructural parameters and nanoparticle content, some mechanical and phisycal properties of the nanocomposite that are affected by nanoparticle content could be directed to microstructure. In the current research, the aim is to study the effect of TiO_2 nanoparticles on polyurethane foam microstructure to find a relation between corresponding parameters such as cell size and foam apparent density. In order to investigate the effect of matrix composition on degree of polymerization and consequently on microstructural evolution of PU foam, two different composition contents of neat PU foam (Isocyanate/Polyol) have been opted.

Experiments

Materials

Semi rigid polyurethane foam used in this study was constituted of two parts (A-side and B-side). A-side was diphenylmethane diisocyanate (MDI) with density of 1.28g/cm^3 and B-side was water containing polyester polyol part with density of 1.20g/cm^3. During process, specific amount of water was added to polyol to react with isocyanate and generate CO_2 gas as foaming agent. TiO_2 nano powders with a purity of 99% and average diameter of about 35 nm were purchased from Nanolina, China.

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Sample Preparation

As declared above, for investigating the effect of matrix composition, two different composition ratios of isocyanate to polyol were chosen. These ratios were selected after testing different composition ratios to seemingly achieve an appropriate stiffness. Selected isocyante to polyol ratios were 1 and 0.7. All nanocomposites samples were produced on the basis of these two composition ratios.

Different weight percents of nano TiO_2 particles (0.02wt%, 0.04wt%, 0.06wt% and 0.2wt%) were selected. In the first step, due to less chemical reactivity of polyol with nano TiO_2 particles and physisorption of OH groups of polyol onto the particle surface, each amount of nanoparticles was mixed into polyol part [4] with 2500 rpm for 5 minutes. The second step was utilization of ultrasonic device to disperse agglomerated nanoparticles in polyol. The ultrasonic disperser device used in this study was Parsonic 2600s (50 watt) with working frequency of 28±5% kHz. The device was filled with ionized water as a sound transmitter media.

Microscopic Evaluation

To characterize the microstructure and determine cell size of the foam, SEM and optical microscopy were used. For characterizing by optical microscopy, thin sheets of PU nanocomposite foams by approximate thickness of 2mm were cut perpendicular to the rising direction. In order to have an image of the porous microstructure by optical microscopy, several images are taken in different focuses and eventually they are merged to have an image. The SEM device (LEO supplied by Zeiss Company) which was utilized for taking images has an accelerating voltage of 35 kV. Sputter coater of Sc 7620 was used to coat a thin layer of gold-palladium on SEM samples for electron discharge.

RESULTS AND DISCUSSION

In Figures (1-a) and (1-b), images of transmitting optical microscopy and SEM of the sample with iso/poly ratio of 1 and nano TiO_2 content of 0.06wt% are included .It is observed that the inner cell walls are visible in transmitting optical microscopy images while in SEM images the outer walls are more noticeable. The outer wall sections are to some extent faded in optical images because of the fact that intensive light passing through the media makes it difficult to observe them which are partly damaged by cutting. To overcome this issue, SEM and optical images of a sample are compared precisely and by this means the outer cell walls become more distinguishable. In Figure (1-a), there is an area in the SEM image that is similar to the one in optical image in which faded walls are clarified. Now that outer cell walls are recognizable, it is reasonable to generalize it to all studied microstructures.

In Figures 2 micrographs of PU closed-cell foams infused with nano TiO_2 particles with composition ratios of 0.7 are shown. The Figures contain micrographs of neat PU foam and nano composite foam samples doped with different nano TiO_2 weight percents of 0.02%, 0.04%, 0.06%, 0.2%. At a glance, it is obviously seen that by increasing the powder content, the cell sizes decrease in both PU compositions. In order to have a better view of cell size distribution, the measuring of average cell sizes can be useful. To determine the cell size of the samples, each cell average diameter in an area of 3.2 mm^2 on the foam surface (area of the corresponding micrograph) is measured and categorized. This measurement is performed for both inner and outer cells that are visible and recognizable in the specified area. A distribution of cell size is plotted for each sample as function of cell numbers in percent. In Figures 3 and 4, cell distribution of some TiO_2 nanocomposites with iso/poly ratios of 0.7 and 1 are illustrated. For clarity of cell distribution trend, some sample results are eliminated from the Figures.

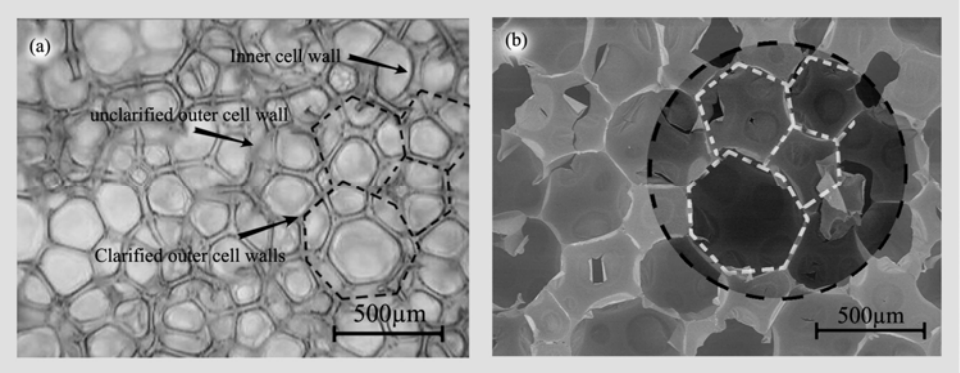

Fig. 1. Clarifying outer cell walls by comparison between (a) transmitting optical microscopy image and (b) scanning electron microscopy image.

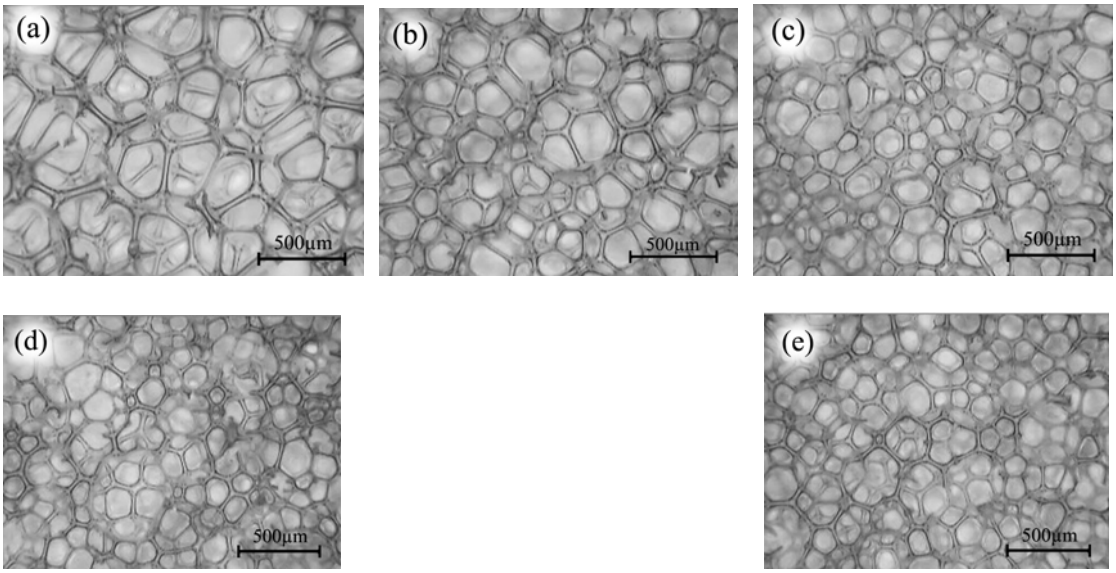

Fig. 2. Microstructures of (a) pure PU foam with iso/poly ratio of 0.7 and nano composite foams infused with (b) 0.02wt% (c) 0.04wt% (d) 0.06wt% and (e) 0.2wt% nano TiO2 particles.

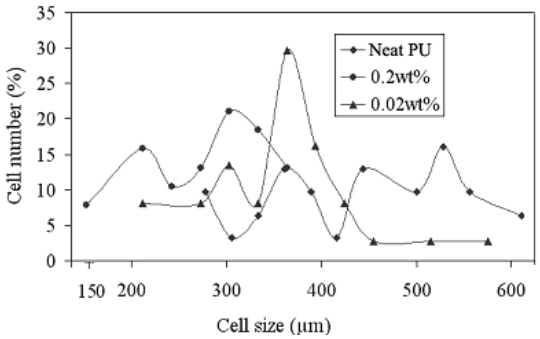

Figure 3: Cell size distribution (ratio 0.7)

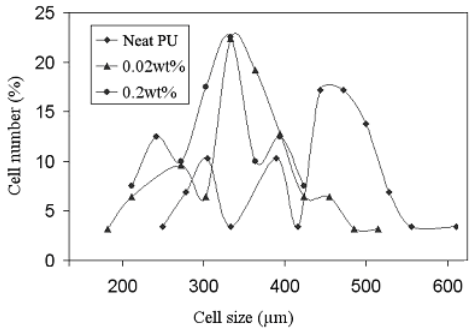

Figure 4: Cell size distribution (ratio 1)

In PU composition ratio of 0.7, the lowest cell size of 150µm is resulted for 0.2wt% nano TiO_2 while by decreasing in particle content up to 0.02wt%, the minimum cell size reaches to 210µm. Peaks in distribution graphs show that there are some dominant cell sizes (from viewpoint of quantity) in each sample. The maximum peak

in samples shifts towards higher cell sizes by adding more particles which is considerable for the sample with 0.02% nano TiO_2.
At 0.2wt% of nano TiO_2, the maximum cell size increases, although it is predicted to be decreased since the nucleating positions increase [5] As a matter of fact 0.2wt% is an abundant amount; a part of this amount acts as bubble nucleants and the surplus is prone to agglomerate and isn't efficient for bubble nucleation. As seen in the Figure, cell size range in the neat PU foam sample is higher than the one in samples doped with different amounts of nano TiO_2 particles. This result shows the effectiveness of nano particles as bubble nucleants.
The cell distribution of some nanocomposite samples with iso/poly ratio of 1 is depicted in Figure 4. As seen, there are some differences in peak altitudes and cell size distribution between two studied ratios. These differences are originated from excess polyol exists in samples with ratio of 0.7. On the one hand excess polyol results in advancement of polymerization reaction and a marked amount of isocyanate is consumed for this reaction. On the other hand for bubble formation reaction, existing water in polyol part reacts with isocyanate to generate CO_2 gas as foaming agent and because of excess polyol, there is surplus amount of water too. Consequently, an increment in the kinetic of bubble generation reaction is resulted. One of two simultaneous sequences is that, some bubbles have been generated are destroyed before cell wall setting. Another sequence is that the existing bubbles become stable in a vast range of cell size due to a rapid polymerization. Because of this fact, in each sample, the difference between peak altitudes of iso/poly ratio of 1 is more than the ones in ratio of 0.7. It is also true to assume that in neat PU foams of both composition ratios the nucleating places are approximately similar; without doping any particles, the only places that are suitable for bubble formation is the mold surface and tiny bubbles that are generated during stirring process of two constituents [6].

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