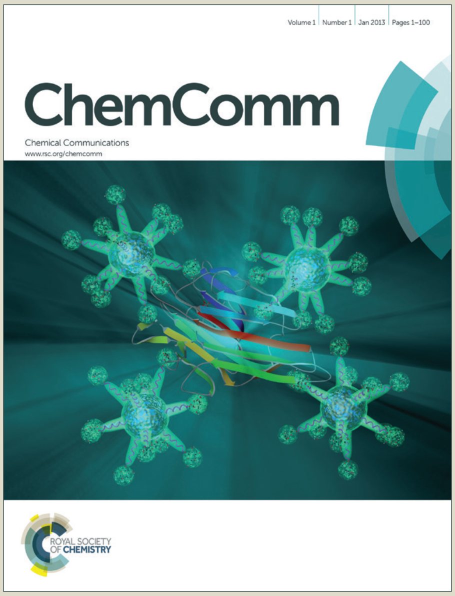
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

The Simplest Method for Fabrication of High Refractive Index Polymer-Metal Oxide Hybrid Based on Soap-Free Process

Hirokuni Jintoku,[a] and Hirotaka Ihara[a,b*]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A new method for facile fabrication of high refractive index material that is based on simple blending of polymer and heteropoly acid is demonstrated. This hybridization is shown to dramatically increase the refractive index of the general polymer, while maintaining a high transparency.

The refractive index (n) of a material is one of the most important factors in determining its suitability for optical applications, which often require a high n value in conjunction with a high transparency. Nowhere is this more evident than in the demands imposed by the industrial production of solar cells, LEDs, OLEDs, optical lenses and filters, anti-reflection films, and optical adhesives.[1]

To meet the urgent and growing needs of these fields, two methods have been developed and proven successful for the fabrication of highly refractive and transparent materials. The first of these is the synthesis of special polymers[2], in which heavy atoms such as sulfur and halogen are incorporated. The other is the blending of metal oxide nanoparticles (NPs) into conventional polymers. In the case of the former, there are advantages in terms of weight and processability when compared with polymer-NPs composite, but inherent limitations in the chemical design render it difficult to achieve an n value of more than 1.8. On the other hand, polymer-NP composites have a high potential for n enhancement, because NPs of TiO_2 and ZrO_2 (with high n values of 2.1–2.7) can be utilized as blending materials.[3] Unfortunately, this also creates serious problems related to the preparation of such nanoparticles, and their adequate dispersion into polymers. Indeed, most nanoparticles have a tendency to agglomerate by themselves in either a solvent or polymer matrix, due to the strong attractive forces between them.[4] Such agglomeration does nothing to increase n, but does have the undesirable effect of increasing the opacity. Therefore, for NPs to be effectively dispersed in a polymer matrix a suitable surface modification or dispersant additive[5] is required; however, such treatments almost invariably cause n to decrease.

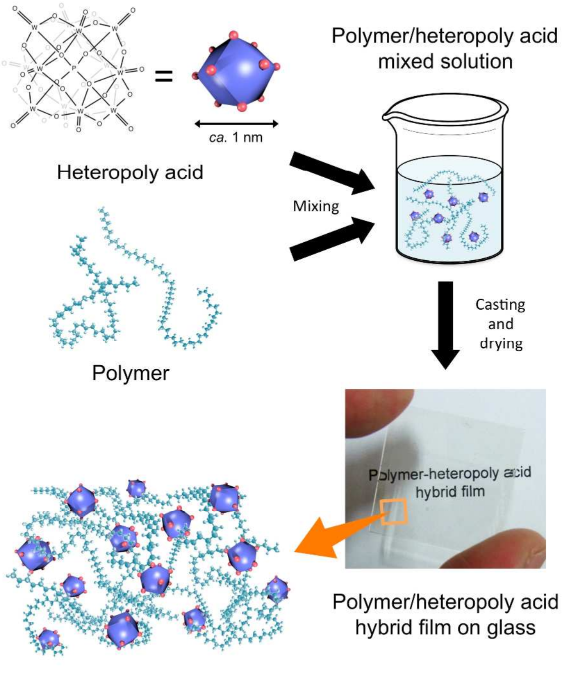


Figure 1. Schematic illustration of the polymer/heteropoly acid hybrid.

To overcome this seemingly insurmountable dilemma, a new strategy is clearly needed for enhancing the n of polymers. To this end, we have made a substantial effort into creating a polymer-supported dispersion of metal oxides, without the use of any additional dispersants; meaning that the polymer must play dual roles as a dispersant and matrix. Our ultimate solution was to use heteropoly acids of tungsten oxide (WO_3), such as 12-

tungstophosphoric acid ($H_3PW_{12}O_{40}$) and 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$), as a colourless and highly refractive index material ($n = 2.2$ as WO_3);[6] a suitable polymer matrix providing the necessary dispersant. The Keggin-type structure of these heteropoly acids provides them with unique chemical, optical and electrical properties.[7] For example, they show good solubility in organic solvents that contain carbonyl, ether or hydroxyl groups, regardless of the fact that WO_3 is not soluble in any organic solvent. Exploiting this unique solubility to hybridize it with polymers presents a number of advantages: (1) a large amount of WO_3 (over 90 wt%) can be incorporated into a given polymer, thus allowing for the possibility of an *n* value of more than 1.9. (2) The *n* value can be easily tuned by changing the ratio of WO_3 to polymer in the initial mixture. (3) The molecular size of heteropoly acid is small enough to diffuse the light that causes opaqueness, but is also readily capable of preventing the agglomeration of WO_3 by hybridizing with polymers. On the basis of these advantages, this paper introduces a new strategy for the controlled fabrication of high refractive index materials that requires no nanoparticles, no dispersant and no substitution with heavy atoms such as halogen in the polymer (Figure 1). We believe that this is the simplest method for fabrication of a high refractive index material and control of refractive index.

A typical example of the hybrid material produced in this study can be seen in the combination of 12-tungstophosphoric acid (PW12) and poly(methyl methacrylate) (PMMA). In this case, both the PMMA and PW12 were dissolved in ethyl acetate to their required concentrations, and then mixed. After stirring for a couple of minutes at room temperature, or until the solution was clear, a solid thin film was obtained by spin coating onto a glass plate. The thickness of this of this film could be readily adjusted within a range of between *c.a.* 50 nm and 10 μm by simply adjusting the concentration and the rotational speed of spin coating. Figure 2 shows the relationship between the PW12concentration in the film and its transmittance loss at 400 nm, as determined by a thermogravimetric (TG) analysis. Typical transmission spectra are shown in the ESI†. From this, we can see that sufficient transparency (defined as less than 5 % transmittance loss) was maintained up to 90 wt% of PW12, although further increase to 93 % PW12 resulted in a turbid film. The transparency is not depending on the thickness of films. However, thick polymer film with high concentration of heteropoly acid (*e.g.* over 85 wt%) causes a decrease of transparency due to not aggregation of heteropoly acid but crack on surface.

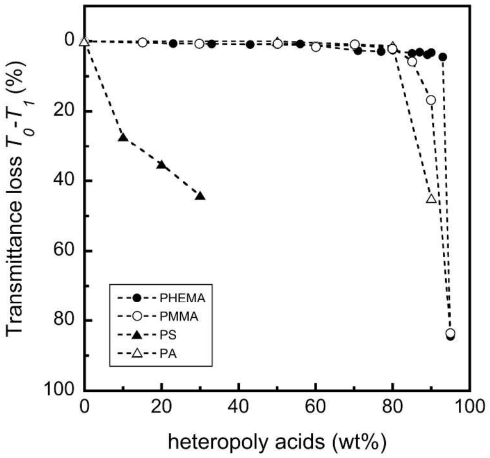


Figure 2. Concentration dependent transmittance losses of polymer/heteropoly acids hybrid film. PHEMA/SiW12 (solid circles), PMMA/PW12 (open circles), PS/PW12 (solid triangles), and PA/PW12 (open triangles). Film thickness = c.a. 3 μm.

A similarly high compatibility with PMMA was observed in the case of using 12-tungstosilicic acid (SiW12) as the metal oxide. Furthermore, it was found that various other polymers could be used instead of PMMA: e.g., poly(hydroxyethyl methaclylate) (PHEMA), poly(acrylate), poly(vinyl acetate), poly(vinyl alcohol) and poly(4-vinylphenol). Unfortunately, non-polar polymers such as polystyrene and polyethylene were not available for comparison (ESI†). Of all the polymers that were tested, an ideal combination of colourlessness and transparency was obtained with a mix of SiW12 (93 wt%) and PHEMA, as shown in Figure 2. Therefore, we believe that this combination is best candidate for creating a colourless and highly refractive polymer thin film.

Figure 3 shows the effect of SiW12 concentration on the refractive index of PHEMA, as determined using a prism coupler (Sairon Technology, Inc., model SPA-4000) equipped with a He-Ne laser (wavelength: 632.8 nm); a method which is suitable for measuring a polymer thin film. The SiW12 content was adjusted from 0 to 93 wt% by altering the initial mixing ratio, revealing a maximum *n* of 1.7810 at 93 wt% SiW12. This value is in the extremely high range for a general-purpose polymer such as PHEMA, but unfortunately no higher value could be achievced. This seems somewhat surprising, given that this value should theoretically reach 1.876 at 93wt% SiW12, regardless of whether the film remains colourless and transparent. In contrast, the observed *n* values of between 1.5053 and 1.6471 obtained for SiW12 values of 0–70 wt% are almost identical to their respective theoretical values (Equation in ESI†), as indicated by the dotted lines in Figure 3. This discrepancy can most likely be explained by the limited control over the surface properties of the film, as well as the presence of water associated with SiW12[8]. Indeed, the values of between 1.6742 and 1.7810 obtained for SiW12 concentrations of 80–93 wt% are much closer to the theoretical values calculated for SiW12 hydrated by six water molecules ($[H_4SiW_{12}O_{40}]\ 6H_2O$) through intermolecular hydrogen bonding.

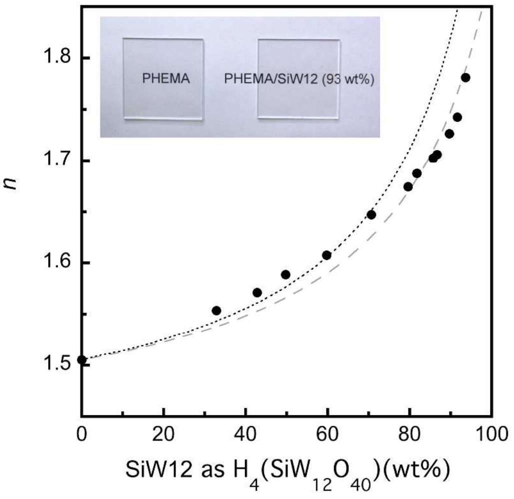


Figure 3. Refractive index of PHEMA/SiW12 hybrid film versus SiW12 concentration. Solid circles: measured refractive index. Dotted line: calculated refractive index as $H_4SiW_{12}O_{40}$. Dashed line: calculated refractive index as $[H_4SiW_{12}O_{40}]\ 6H_2O$. The inset picture shows photo images of PHEMA and PHEMA/SiW12 coated glass plate.

Since these hydrogen bonds with water can be disrupted by thermal treatment at 140-260 ˚C[8], this presents a means by which the *n* value can be increased. With this in mind, a PHEMA/SiW12 (80 wt%) film prepared from a MeOH/DMF (2:1) mixed solution was subjected to thermal treatment at 180 ˚C for 2 hours; exhibiting an increase of *n* from 1.6742 to 1.7151. Moreover, the *n* value remained consistent with the theoretical value up to 80 wt% SiW12 (ESI†). However, above this concentration the *n* value remained closer to the theoretical value of $[H_4SiW_{12}O_{40}]\ 6H_2O$. By substituting PMMA and PW12 for the PHEMA and SiW12, respectively, a similar increase of *n* was observed; however the maximum *n* of 1.7544 was detected at 90 wt% PW12 (ESI†).

Interestingly, this PHEMA/SiW12 film exhibited a low haze (i.e., a low angular dependency against incident light), which is one of the most important essential properties of a transparent film. Indeed, the haze of the PHEMA/SiW12 (80 wt%) film was found to be less than 1 %. To explore the reason of low haze, the dispersibility of SiW12 in the PHEMA/SiW12 film was analyzed by energy dispersive X-ray (EDX) and transmission electron microscopy (TEM). The resulting EDX images of the carbon and tungsten concentration in the PHEMA/SiW12 (80 wt%) film, as shown in Figure 4(a,b), reveal that a high concentration and dispersion of tungsten was achieved in the film (ESI†). Furthermore, in the accompanying TEM images (Figure 4c, d), no large agglomerated structure can be observed at either concentration of SiW12 (20 and 80 wt%). The surface morphology of the films was also evaluated by atomic force microscopy (AFM), with the resulting 2D and 3D images of PHEMA/SiW12 (80 wt%) confirming a uniform surface without any discernible agglomeration (ESI†).

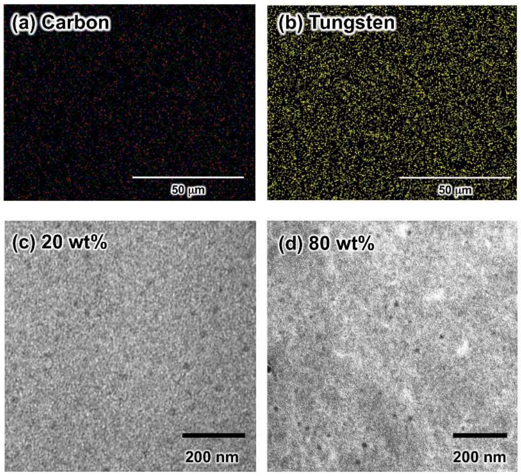


Figure 4. EDX mappings of (a) carbon and (b) tungsten in the PHEMA/SiW12 (80 wt%) hybrid film. TEM images of (c) PHEMA/SiW12 (20 wt%) and (d) PHEMA/SiW12 (80 wt%) hybrid films.

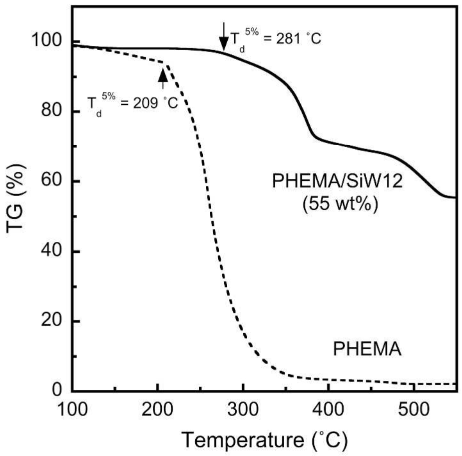


Figure 5. TG curves of PHEMA and PHEMA/SiW12 (55 wt%) hybrid. The PHEMA/SiW12 (55 wt%) film was prepared from a MeOH/DMF (2 : 1) mixed solvent.

The mechanism behind the hybridization of the PMMA/PW12 and PHEMA/SiW12 mixtures was analyzed through FT-IR and XRD spectroscopy. The FT-IR spectra of the PMMA/PW12 film (20–90 wt%) showed a significant shift in the peak associated with C=O stretching vibration (ESI†). That is, when the concentration of PW12 is increased, $\nu_{C=O}$ is shifted to a shorter wave number (1729 cm^{-1} to 1697 cm^{-1}) due to the intermolecular hydrogen bonding between carbonyl moieties of PMMA and PW12. In contrast, no such peak shift is observed in the C=O band ($\nu_{C=O}$: 1719 cm^{-1}) of the PHEMA/SiW12 (20–90 wt%) film (ESI†); however, the H-O-H bending band of SiW12 and –OH stretching band of PHEMA do exhibit a shift to a longer wave number ($\delta_{H\text{-}O\text{-}H}$: 1586 to 1604 cm^{-1} and $\nu_{\text{-}OH}$: 3408 to 3556 cm^{-1}) due to hydrogen bonding between the hydroxyl moieties of PHEMA and PW12 (ESI†).[7c, 9] These results indicate that the interaction between a heteropoly acid and a polymer is entirely dependent on the structure of the polymer in question. Nevertheless, as shown in XRD patterns of the PMMA/PW12 and PHEMA/SiW12 films, the heteropoly acids are dispersed in their respective polymer matrixes (ESI†). Hybridization is confirmed by the broadening of small-angle peaks (θ = 6–10˚), which are attributed to a second order structure of PW12 and SiW12[7a, 10], thus indicating that the heteropoly acids exist as a well-dispersed amorphous phase. FT-IR and XRD spectra indicate that the heteropoly acids could form complexes with direct interaction and disperse in polymer matrices as amorphous state.

This hybridization of SiW12 not only increases the refractive index, but also affects the thermal stability, water-resistance and surface hardness. From the results of the TG analysis (Figure 5), it is clear that the weight loss temperature ($T_d^{5\%}$) of the PHEMA/SiW12 (55 wt%) hybrid is notably higher than that of PHEMA alone. This thermally-stable film was obtained by either the addition of amide solvents (dimethylformamide (DMF) and dimetylacetamide) or an alkali solution (*e.g.* NaOH *aq.*), combined with thermal treatment at 180 ˚C for 30 min. PHEMA/SiW12 (55 wt%) film can keep colourless and transparent until 200 ˚C. However, thermal treatment at 250 ˚C changes the film colour to dark brown (ESI†). The thermal-stable hybrids exhibited water- and organic solvent-resistant. No or slight weight changes were observed by immersion treatment of PHEMA/SiW12 (55 wt%) hybrid in water, methanol and ethyl acetate for a day at 25 ˚C. The surface hardness of PHEMA/SiW12 (50 wt%) hybrid on a glass substrate (6H) is also greater than that of PHEMA alone (2H).[11] The surface hardness of films was measured by the pencil hardness test that was measured under the same conditions including the film thickness (5 μm), the kinds of substrate (glass), and the load (750 g). And the judgment of the hardness was detected by the presence or absence of the scratches of the film surface. Such enhancements in the mechanical properties of these hybrid films opens the possibility for the use as a surface coating or an optical lens.

The results presented establish a new strategy for creating a highly refractive material from a hybrid of heteropoly acids and polymer. This provides obvious advantages, in that eliminates the need for nanoparticles or chemical dispersants. A PHEMA film incorporating 93 wt% SiW12 demonstrated both a high refractive index (*n* = 1.7810) and a high transparency (T% = 88 % at 400-700 nm). Furthermore, this hybrid film also exhibited enhanced mechanical properties, such as a high thermal stability and high surface hardness. This therefore provides considerable insight into the creation of new highly-refractive materials, with investigation ongoing into further improvements in the refractive index, thermal stability, and other optical and mechanical properties.

This work was supported by a Grant-in-Aid for Program for Regional Innovation Strategy Support Program from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

[a] *Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555 (Japan), Tel/Fax: (+81)96-342-3662, E-mail: ihara@kumamoto-u.ac.jp*
[b] *Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Kumamoto, 862-0901 (Japan)*

† Electronic Supplementary Information (ESI) available: Transmission, FT-IR, EDX, and XRD spectra, refractive index, and AFM images of polymer/heteropoly acid hybrids. See DOI: 10.1039/c000000x/

1 (a) M. Schraub, H. C. Kim and N. Hampp, *Eur. Polym. J.*, 2014, **51**, 21; (b) J. Moghal, S. Reid, L. Hagerty, M. Gardener and G. Wakefield, *Thin Solid Films*, 2013, **534**, 541; (c) P. S. Kollbaum, A. Bradley and L. N. Thibos, *Optom. Vis. Sci.*, 2013, **90**, 924; (d) M. Müller, R. Zentel, T. Maka, S. G. Romanov and C. M. S. Torres, *Adv. Mater.*, 2009, **12**, 1499; (e) T. Komikado, A. Inoue, K. Masuda, T. Ando and S. Umegaki, *Thin Solid Films*, 2007, **515**, 3887.
2 (a) C. Paquet, P. W. Cyr, E. Kumacheva and I. Manners, *Chem. Commun.*, 2004, 234; (b) C. K. Jim, J. W. Lam, A. Qin, Z. Zhao, J. Liu, Y. Hong and B. Z. Tang, *Macromol. Rapid Commun.*, 2012, **33**, 568; (c) Y. C. An and G.-i. Konishi, *J. Appl. Polym. Sci.*, 2012, **124**, 789; (d) Y. Nakagawa, Y. Suzuki, T. Higashihara, S. Ando and M. Ueda, *Macromolecules*, 2011, **44**, 9180; (e) M.-C. Choi, J. Wakita, C.-S. Ha and S. Ando, *Macromolecules*, 2009, **42**, 5112; (f) H. Kudo, H. Inoue, T. Nishikubo and T. Anada, *Polym. J.*, 2006, **38**, 289; (g) B. Liu, W. Hu, Y. Jin, C. Chen, Z. Jiang, Z. Wu, T. Matsumoto and A. Matsumura, *Macromol. Chem. Phys.*, 2004, **205**, 1677.
3 (a) C. Lü and B. Yang, *J. Mater. Chem.*, 2009, **19**, 2884; (b) M. Wong, J. Guenther, L. Sun, J. Blümel, R. Nishimura and H.-J. Sue, *Adv. Funct. Mater.*, 2012, **22**, 3614; (c) P. Tao, Y. Li, A. Rungta, A. Viswanath, J. Gao, B. C. Benicewicz, R. W. Siegel and L. S. Schadler, *J. Mater. Chem.*, 2011, **21**, 18623; (d) T. Tamai, M. Watanabe, Y. Minami, S. Okazaki, A. Masuyama and K. Matsukawa, *Chem. Lett.*, 2011, **40**, 37; (e) T. Otsuka and Y. Chujo, *Polymer*, 2009, **50**, 3174; (f) M. H. Ullah, J.-H. Kim and C.-S. Ha, *Mater. Lett.*, 2008, **62**, 2249; (g) J. L. H. Chau, Y.-M. Lin, A.-K. Li, W.-F. Su, K.-S. Chang, S. L.-C. Hsu and T.-L. Li, *Mater. Lett.*, 2007, **61**, 2908.
4 (a) M. Jose and M. Sakthivel, *Mater. Lett.*, 2014, **117**, 78; (b) M. R. Noor El-Din, I. M. El-Gamal, S. H. El-Hamouly, H. M. Mohamed, M. R. Mishrif and A. M. Ragab, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2013, **436**, 381; (c) T. E. Kodger and J. Sprakel, *Adv. Funct. Mater.*, 2013, **23**, 475.
5 (a) J. Guo, W. Yang and C. Wang, *Adv. Mater.*, 2013, **25**, 5196; (b) P. Akcora, H. Liu, S. K. Kumar, J. Moll, Y. Li, B. C. Benicewicz, L. S. Schadler, D. Acehan, A. Z. Panagiotopoulos, V. Pryamitsyn, V. Ganesan, J. Ilavsky, P. Thiyagarajan, R. H. Colby and J. F. Douglas, *Nat. Mater.*, 2009, **8**, 354; (c) Y. Min, M. Akbulut, K. Kristiansen, Y. Golan and J. Israelachvili, *Nat. Mater.*, 2008, **7**, 527.
6 K. J. Lethy, D. Beena, R. Vinod Kumar, V. P. Mahadevan Pillai, V. Ganesan and V. Sathe, *Appl. Surf. Sci.*, 2008, **254**, 2369.
7 (a) M. B. Colovic, D. V. Bajuk-Bogdanovic, N. S. Avramovic, I. D. Holclajtner-Antunovic, N. S. Bosnjakovic-Pavlovic, V. M. Vasic and D. Z. Krstic, *Bioorg. Med. Chem.*, 2011, **19**, 7063; (b) M. Hashimoto, G. Koyano and N. Mizuno, *J. Phys. Chem. B*, 2004, 12368; (c) M. KLISCH, *J. Sol-Gel Sci. Technol.*, 1998, **12**, 21. (d) D. E. Katsoulis, *Chem. Rev.*, 1998, **98**, 359
8 N. Essayem, Y. Y. Tong, H. Jobic and J. C. Vedrine, *Appl. Catal., A*, 2000, **194**, 109.
9 T. J. Kashi, M. Erfan and D. Watts, *Journal of Dentistry, Tehran University of Medical Sciences*, 2007.
10 (a) X. Zhao, H.-M. Xiong, W. Xu and J.-S. Chen, *Mater. Chem. Phys.*, 2003, **80**, 537; (b) J. A. Dias, E. Caliman and S. C. Loureiro Dias, *Microporous Mesoporous Mater.*, 2004, **76**, 221; (c) L. G. Bach, M. R. Islam, S. Y. Seo and K. T. Lim, *J. Appl. Polym. Sci.*, 2013, 261.
11 C.-C. Chang, T.-Y. Oyang, F.-H. Hwang, C.-C. Chen and L.-P. Cheng, *J. Non·Cryst. Solids*, 2012, **358**, 72.