

Synthesis and Characterization of Titanium Dioxide Optical Films by Sol–Gel Processes

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ABSTRACT: The main purpose of this study is to synthesize the front panel of monitor with a high refractive index optical film. Our experiment uses titanium dioxide nanoparticles mixed with methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (2-HEMA), and tri(ethylene glycol) dimethacrylate (TEGDMA) of the wet type and economical sol–gel production process. Our product has a superior mechanical, thermal, and optical properties was demonstrated by Fourier transform infrared spectrum (FTIR), differential scanning calorimeter (DSC), thermogra-

vimetric analysis (TGA), UV/visible spectrum, and Spectro Ellipsometer. In addition, we found the surface of the two series of thin film with the organic and inorganic high refractive index (TiO_2) mixed materials, has high transmittance for visible light above 90%, refractive index <1.65 and the hardness test 6H. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2271–2280, 2007

Key words: thin films; hardness; inorganic polymers; photochemistry; refractive index

INTRODUCTION

It is well-known that transition metal alkoxides are highly reactive chemical compounds.¹ These compounds react vigorously in an alcoholic medium through hydrolysis–condensation reactions to form polymers which grow into an inorganic network. By controlling the hydrolysis and condensation reaction, it is possible to obtain a gel or a precipitate which, by carefully controlled drying and sintering processes, lead to a bulk mass or powder. However, in some cases, the hydrolysis reaction is not complete and unhydrolyzed alkoxide groups remain in the resulting product.^{2,3} This is seen in the case of titanium alkoxides. Several studies suggest that hydrolysis occurs rapidly whereas the condensation reaction is slow for titanium alkoxides.⁴ The slower condensation reaction that succeeds the hydrolysis reaction ultimately results in the precipitation of titanium dioxide, TiO_2 .

A series of polymer–titania hybrid materials, including TiO_2 -poly(arylene ether ketone),⁵ TiO_2 -poly(methyl methacrylate),^{6,7} and TiO_2 -aminoalkoxysilane capped-pyromellitic dianhydride,⁸ have been thoroughly studied using this method. These hybrid materials combine the advantages of organic polymers (lightweight, flexibility, good impact resistance, and good processability) and inorganic materials (good

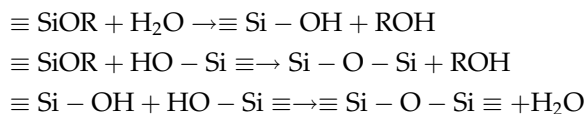
chemical resistance, high thermal stability, and high brittleness). Furthermore, the refractive index of the hybrid materials can be easily manipulated via adjusting the ratio of inorganic phase to organic phase.^{9–11}

Hybrid materials have been extensively used in the photoelectric materials domain. In addition to being used in antireflection (AR) front panels, liquid crystal display (LCD), laser discs, and mobile phone housings,^{12,13} it is also used in construction, medical, and transportation tools. When the external light is strong, the surface glass of a LCD monitor screen appearing glare and reducing the quality of the display. Thus, its performance is decreased greatly in public places with bright outdoor lighting. The best way to overcome this problem is to use surface treatments. The preparation of antireflection coated film has become a necessity, there are tradeoffs, to be considered, enhancing the antireflection properties of the materials will also affect their refractive index. Thus, to produce material with desirable antireflection properties, it is imperative to research and discuss the refractive index link.

The hybrid material is formed from the combination of two or more kinds of materials. Depending on the natural characteristics of the material used in each group, the advantages of each group can be individually shown, bringing out complementary effects.⁵ To meet emerging needs, a hybrid material is generally formed from the combination of a basic matrix material and a reinforcing material. In addition to the inherent properties of the materials, the condition, surface nature, and particle size also influence the

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characteristic of the final product. As the particle size is reduced, the hybrid effect and contact surface effort are greatly improved and enhanced. The sol-gel process uses alkoxide compound as precursor, of which the most commonly used is tetraethoxysilane (TEOS), and through hydrolysis, the siloxane group bond is created. Siloxane bond is formed through condensation polymerization, creating alcohol and water as by-products. The hydrolytic and polymeric reactions by three-step are described as follows:



where R is C_2H_5 . When the siloxane content is continuously increased, the sol granules were formed, and the reaction would occur under suitable conditions, these sol granules agglutinate into the gel.¹⁴ The abovementioned hydrolysis and condensation steps are affected by different factors such as $\text{H}_2\text{O}/\text{TEOS}$ content ratio, kinds of catalysts, and reaction temperature, which influence the ultimate mechanical properties of the product.¹⁵

Since poly(methyl methacrylate) (PMMA) has a stable physical and chemical nature, it has been extensively used in recent years.¹⁶ For example, it is used as a protective layer for LCD displays. It is also used as an abrasion-resistant and heat resistant photoelectric material component, and it can be reformed into uniform, smooth, and even thin film. When mixed with a coupling agent, e.g., 2-HEMA (2-hydroxyethyl methacrylate monomer), it can become a highly transparent resin.^{17,18}

The sol-gel process in preparing inorganic/organic hybrid materials has been used by several researchers. Hydrogen bonding of hybrid material and, followed by, covalent bonding are the two steps in the inorganic-organic reaction. The main reason for using sol-gel process in inorganic/organic hybrid material synthesis is because the inorganic network structure of sol-gel provides outstanding optical properties for the hybrid materials.¹⁹

The synthesis route mainly uses the wet type and economical sol-gel production process, which uses titanium dioxide nanoparticles mixed with MMA, 2-HEMA, and TEGDMA.^{4,8,20} The monomer triethylene glycol dimethacrylate (TEGDMA) is a common component of both bonding and resin composites often used for dental materials. A TEGDMA-containing resin composite hastened and increased TEGDMA diffusion through dentine.²¹ A composite containing greater amounts of TEGDMA showed a greater degree of conversion. The amount of postirradiation polymerization decreased as the content of the incorporated TEGDMA increased.²¹ Further, it showed

that substitution of TEGDMA by UEDMA (Urethane dimethacrylate) resulted in an increase in tensile and flexural strength, and that substitution of BisGMA (bisphenol-A-glycidyl dimethacrylate) by TEGDMA increased tensile, but reduced flexural strength.²²

In this study, silicon dioxide particles mixed with acrylic series monomers, with an unsaturated bond are used. The methyl methacrylate, 2-HEMA (2-hydroxyethyl methacrylate monomer) and TEGDMA are used as a bonding resin by sol-gel process for preparing inorganic-organic hybrid materials (Table I). The purpose of this study was to know how the effect of TEGDMA on this hybrid material affected the optical, mechanical, and thermal properties.

EXPERIMENTAL

Materials

Titanium(IV)*n*-butoxide (TBOT, 99%, ACROS), acetylacetone (AcAc, Wako Pure Chemical Industry Co., Japan), 2-propanol (IPA, Kanto Chemical Co.), methyl methacrylate (MMA, Kanto Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Kanto Chemical Co.), tri(ethylene glycol) dimethacrylate (TEGDMA, ALDRICH), and hydrochloric acid (HCl, Osaka Chemical Co., Japan) were used for the synthesis of hybrid thin film.

Instruments

Fourier transform infrared spectrum

Infrared spectra of the hybrid materials were obtained using a Fourier transform infrared spectrum (FTIR, Nicolet model 320), whose resolution is about 8 cm^{-1} and the scanning number is 32 in the 4000–400 nm range. Before using the FTIR, potassium bromide (KBr) powder is placed in the vacuum oven to remove its water, and then it is ground into fine powder, using the agate earthen, and placed into mixing/slicing machine and pressed into a spindle. Using potassium bromide salt as background check,

TABLE I
Compositions of the Prepared the Organic/Inorganic Hybrid Materials

Code no.	Inorganic (g)	MMA (g)	2-HEMA (g)	TEGDMA (g)	Initiator (g)
10Ti110	5.26	2.37	2.37	—	1.58
30Ti110	8.10	0.95	0.95	—	0.63
50Ti110	9.09	0.45	0.45	—	0.30
70Ti110	9.59	0.21	0.21	—	0.14
90Ti110	9.89	0.06	0.06	—	0.04
10Ti111	5.26	1.58	1.58	1.58	1.58
30Ti111	8.10	0.63	0.63	0.63	0.63
50Ti111	9.09	0.30	0.30	0.30	0.30
70Ti111	9.59	0.14	0.14	0.14	0.14
90Ti111	9.89	0.04	0.04	0.04	0.04

and with the spin coated method, the sampling produced from the reaction is dropped into the potassium bromide salt slice to undergo testing.

Differential scanning calorimeter

About 4–5 mg of the sample is paced in an aluminum spindle. These samples were conducted using differential scanning calorimeter (DSC, DuPont model TA-2010), under dry nitrogen at a heating rate of 20°C/min and temperature from –80°C to 200°C.

Thermogravimetric analysis

About 8–10 mg of sample is placed in the hanging basket for weighing, and thermogravimetric analysis (TGA, DuPont model 951) was done under a dry nitrogen atmosphere over a temperature range of 30 to 800°C at a heating rate of 20°C/min.

UV/visible spectrum

The sample to be tested is spread on the glass slide using the spin-coated method, and two empty glasses slide are also placed in the sample trough to carry out empty check. Finally, the slide spread with sample is placed inside the sample trough to undergo testing (UV/vis, Jasco model V-530); visible light scanning wavelength was set in the range of 400–800 nm.

Spectro ellipsometer

A Spectro Ellipsometer analyzer (Sopra, model GESP5) was used to measure the refractive index (*N*) of the prepared films in the wavelength range of 190–900 nm.

Preparation of inorganic/organic hybrid materials

To prepare inorganic/organic high refractive index hybrid solutions (C) are obtained to undergo reaction with various amount of organic solution (A), inorganic solution (B), and 1 wt % initiator at room temperature for 30 min. Preparation of organic solution (A) carried out in different ratio of MMA, 2-HEMA, TEGDMA in a three-necked flask at room temperature for an hour. In addition, the inorganic solution (B) was prepared by mixing TBOT, catalytic agent, HCl, IPA solvent, AcAc, and distilled water with an ice bath for 5 h. Finally, high refractive index thin films were deposited with the hybrid solutions (C) by spin-coating on the glasses as substrates in the control of the rotation speed below 3000 rpm for 30 s. Then, the thin films were cured under UV light. The experimental flow chart is shown in Figure 1.

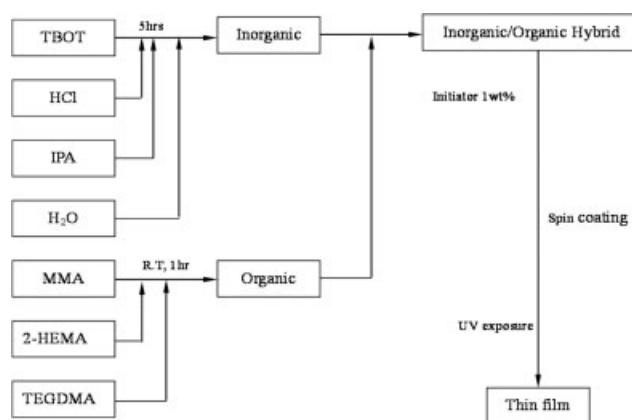


Figure 1 The preparation of the synthetic procedure of the organic/inorganic hybrid materials.

RESULTS AND DISCUSSION

Structural analysis

The light assembling characteristics of organic/inorganic high refractive index TiO₂ hybrid material can be formed into stable and half stable quantitative analysis using the FTIR spectra. Each molecular bond absorption area is shown in Figures 2 and 3. The absorption bands includes including C=C bond stretching vibration ($\lambda = 1680$ nm), C=O bond stretching vibration absorption ($\lambda = 1730$ nm), C–H bond of methyl asymmetric scissoring vibration absorption ($\lambda = 1455$ nm), O–H stretching vibration absorption ($\lambda = 3409$ nm), –OH bond bending vibration ($\lambda = 1650$ nm), and Si–OH bond stretching vibration absorption ($\lambda = 921$ nm). The above-mentioned functional groups base can be confirmed in the literature.^{6,7,17,18}

It can be noted from Figure 4 that absorption peak of monofunctional base acrylic monomer MMA and C=C bond of coincidental agent, 2-HEMA became small after UV exposure. There were obvious remnants of double bond absorption. This was because of free-radical polymerization. Its reaction rate was considerably fast. Within a short period of time, the organic part formed network bonding, making it difficult for the monomer to complete polymerization, there by causing band C=C to have extremely few remnants.²³ The 3400–3500 nm bands belonging to the absorption peak of coincidental agent and water has become evidently small after UV exposure, and with few remnants.

It can be seen from Figure 5 that with the addition of a crosslinking agent, TEGDMA, into monofunctional base of acrylic monomer MMA and 2-HEMA. C=C absorption peak after UV exposure had completely disappeared, suggesting that C=C bond had initiated the reaction.

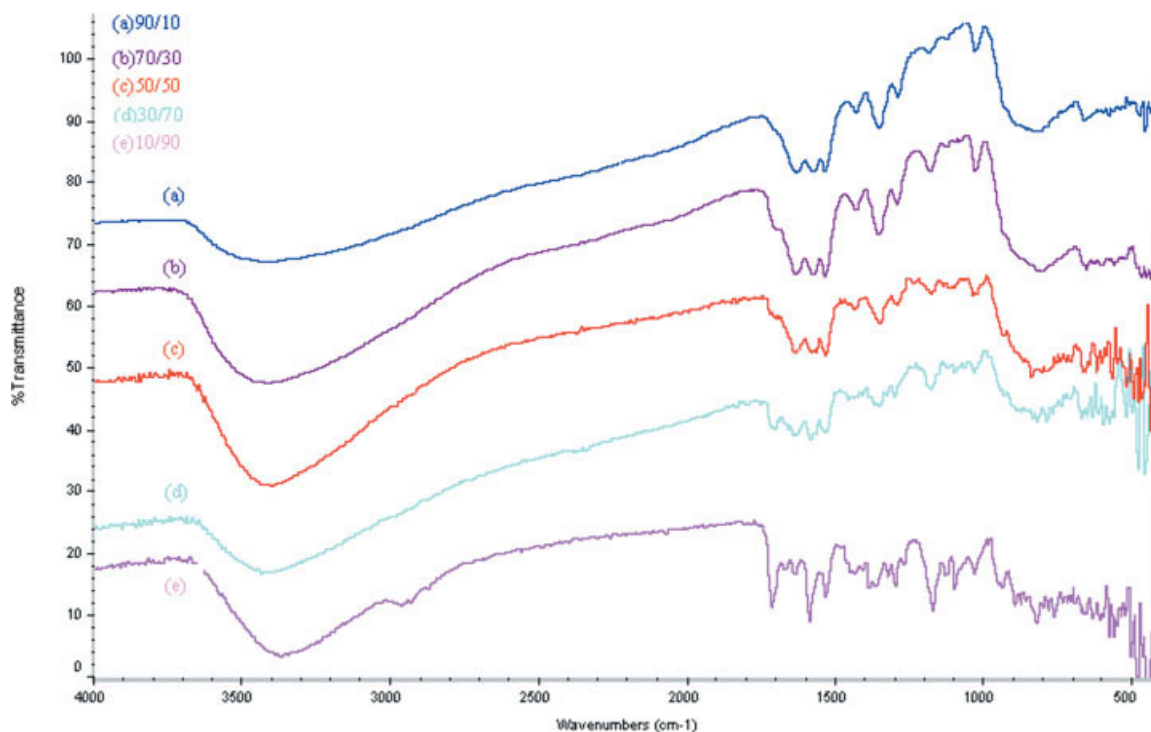


Figure 2 The FTIR spectra of titanium dioxide mixed with two monomer series were unexposure of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

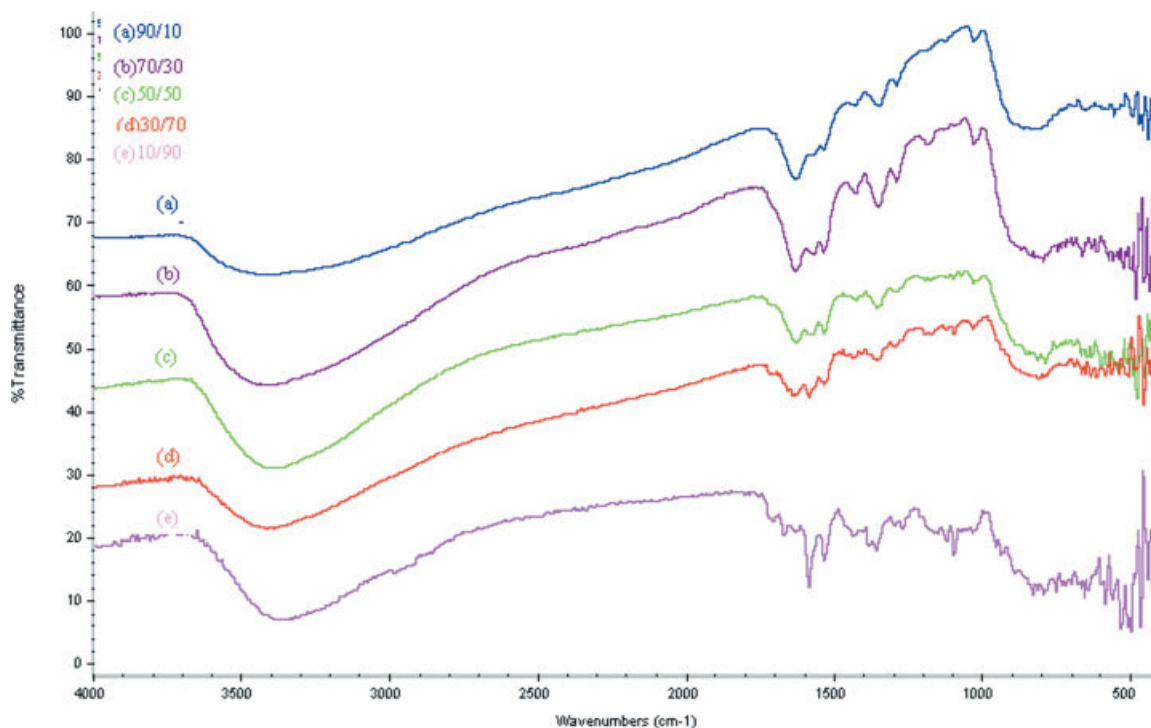


Figure 3 The FTIR spectra of titanium dioxide mixed with two monomer series were exposure of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

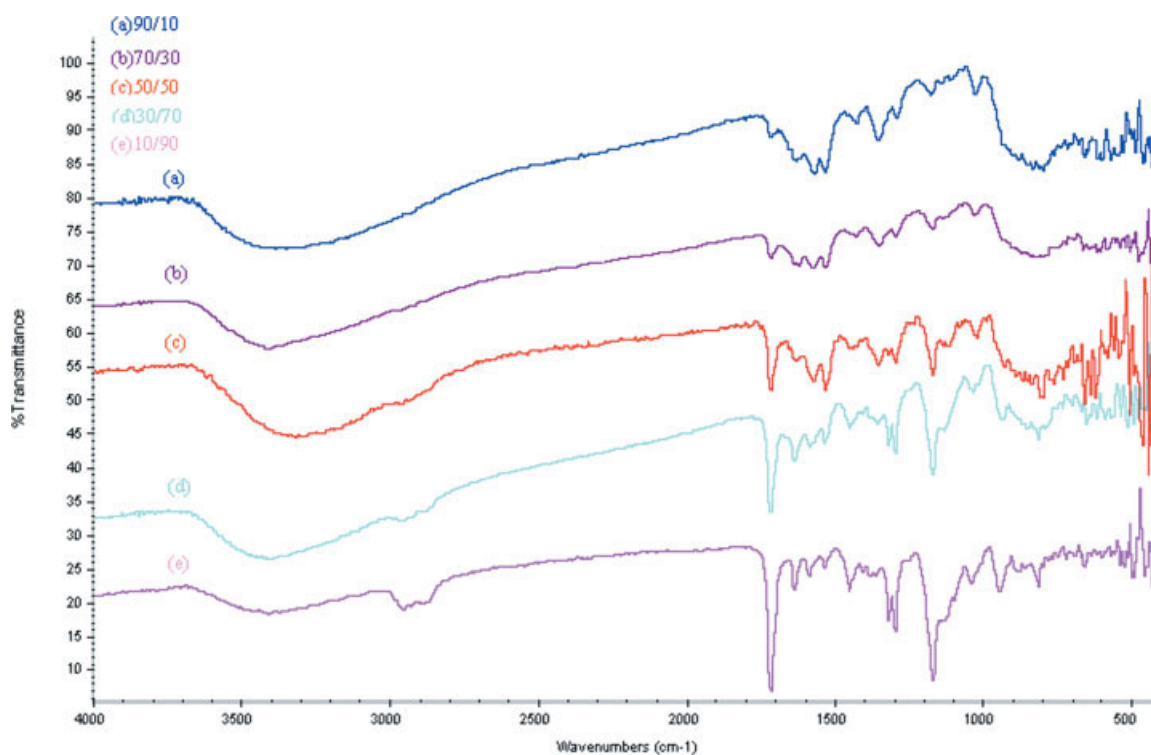


Figure 4 The FTIR spectra of titanium dioxide mixed with three monomer series were unexposure of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

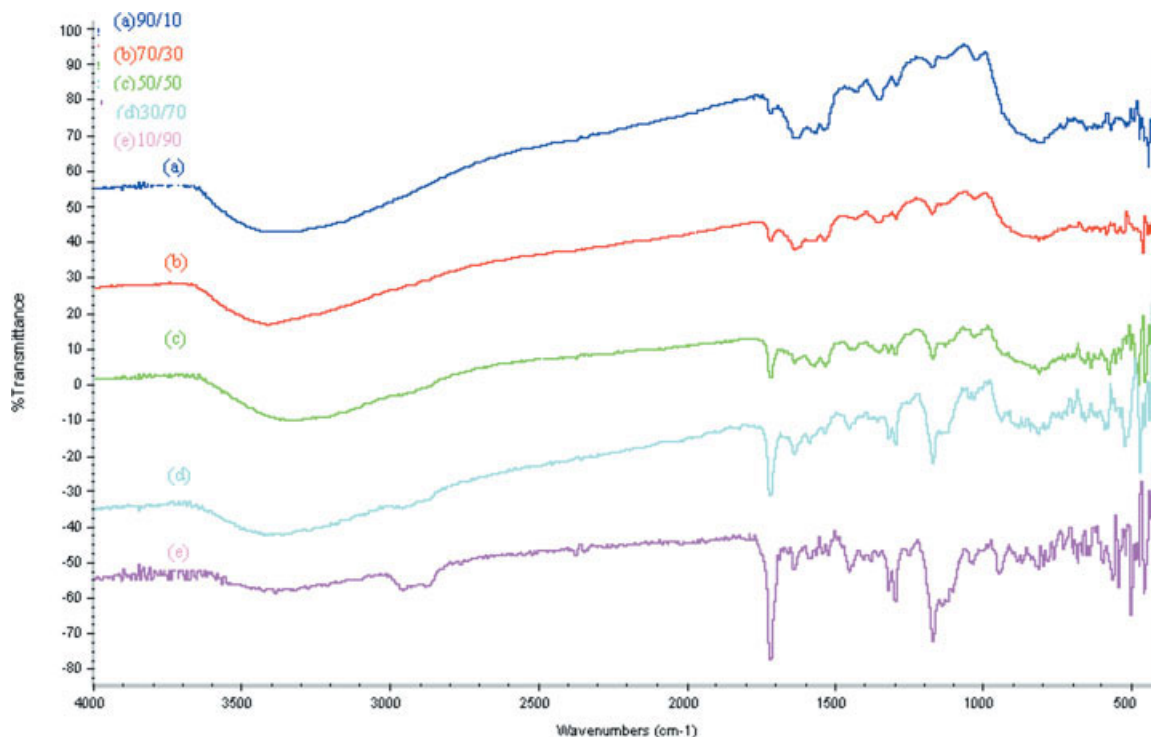


Figure 5 The FTIR spectra of titanium dioxide mixed with three monomer series were exposure of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
The Transmission T (%) (550 nm) and Refractive Index N of the Organic/Inorganic Hybrid Materials

Code no.	N	T (%)
10Ti110	1.479	94.953
30Ti110	1.473	95.393
50Ti110	1.473	95.583
70Ti110	1.468	95.901
90Ti110	1.468	96.225
10Si111	1.484	93.960
30Si111	1.476	95.012
50Si111	1.448	95.583
70Si111	1.444	96.107
90Si111	1.439	96.402

Optical characterization

This experiment uses the UV/vis and Spectro ellipsometer to confirm the light transmittance and refractive index of inorganic/organic high refractive index TiO_2 hybrid material. Results are shown in Table II. It can be noted from the UV/vis absorption feature that the transparency of inorganic/organic high refractive index TiO_2 hybrid mixture produced in this research is good (Figs. 6 and 7). It also shows excellent optical permeability nature and good dispersal nature of titanium dioxide in an organic basic material.

Since optical element is very important in the light visibility area of transparency nature, it is needed closed to 90%. This can be seen in Figure 1. The requirement of optical element in the production of thin film in this research can be noted from the chart. This research uses nanoscale titanium dioxide particles because the size is small and cannot seriously cause the light scattering, thereby possessing high transparency nature. In addition, the monofunction base acrylic monomer MMA and 2-HEMA at UV area starts to have absorption; thus, absorption of thin film at UV wavelengths increase decreasing the transparency. It can also be noted from the chart that the transparency will increase upon increasing the TiO_2 concentration.^{24–26}

Mechanical properties

This experiment was conducted under the ASTM D3363-74 standard pencil hardness test to confirm the change of the hardness on the film after the addition of crosslinking agent, TEGDMA. The standard index is from HB, F, H, 2H, 3H, 4H, 5H, and 6H. The HB is soft, and 6H is hardness of the test.²⁷ Using the already known hardness of pencil to analyze thin film, the hardest pencil number that could not scratch the film would be the hardness of the film. It can be noted

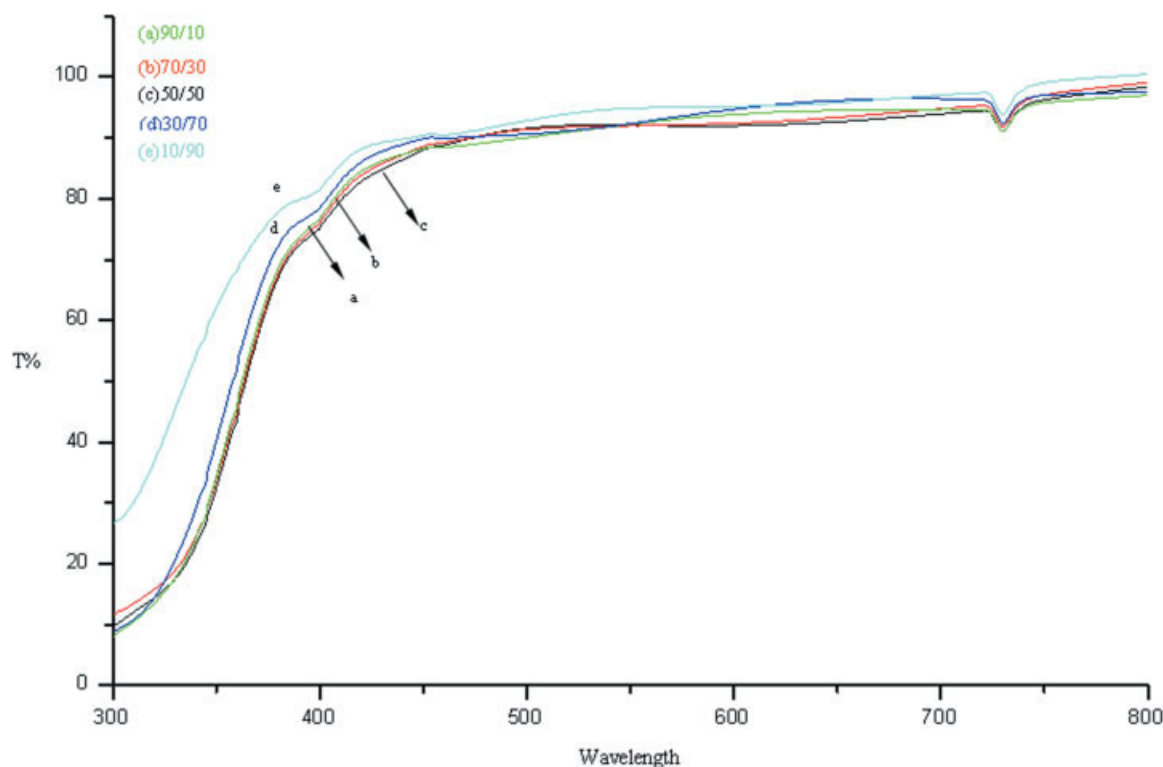


Figure 6 The UV/vis spectra of titanium dioxide mixed with two monomer series of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

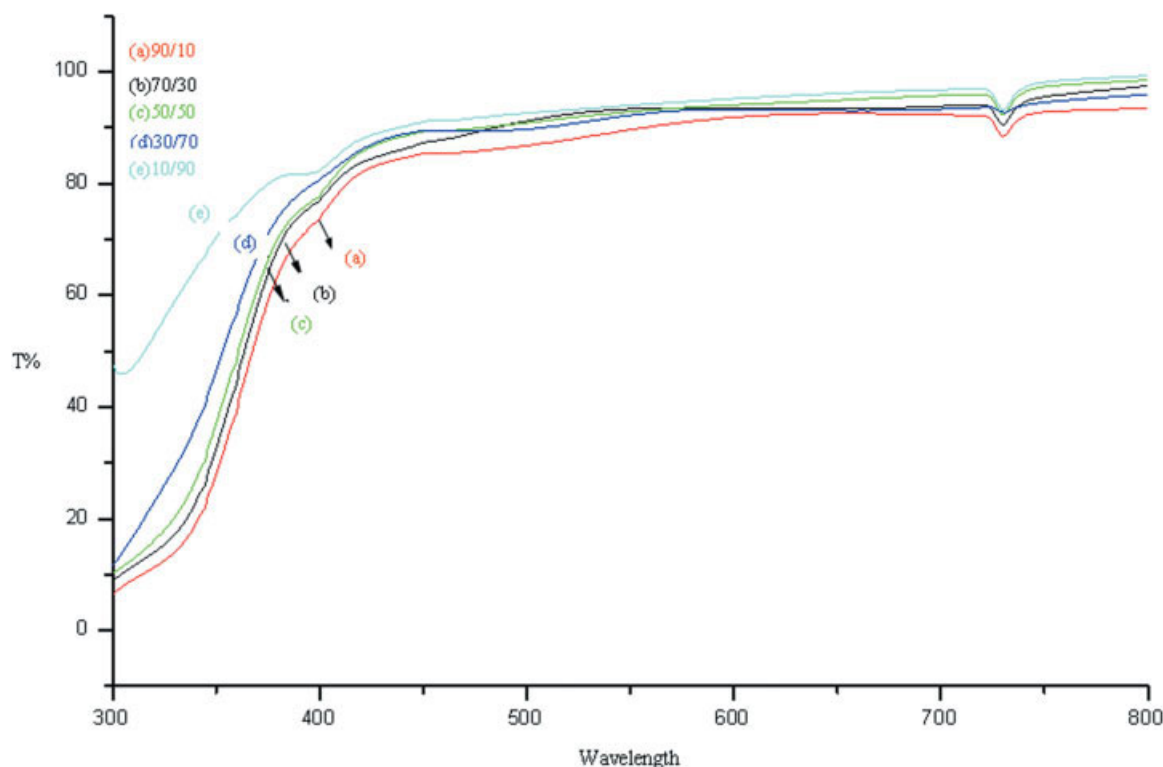


Figure 7 The UV/vis spectra of titanium dioxide mixed with three monomer series of hybrid inorganic/organic materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

from Table III that the addition of TEGDMA elevated the hardness, which was beneficial, and the thin film produced in this experiment obtained the best pencil hardness test result of 6H. Comparing the hardness of the two series, when the amount of organic solution reached 50%, pencil hardness test increased along with the increase in the content of TEGDMA, which showed that the above-said matter provided a highly concentrated double bond during reaction, thus, creating covalent bond and the formation of organic network construction, and elevating mechanical properties of inorganic/organic hybrid mixture.

Thermal stability

The TGA charts are shown in Figures 8 and 9, where it can be observed that the system has three separately stages of gravity loss. In the first stage between 100 and 150°C, it is due to the combustion of solvent, water and catalyst or nonreactive monomer. In the second stage between 350 and 450°C, it is due to the combustion of C, H, and O compounds. In the third stage above 500°C, it is due to the degradation of organic compounds in this material. It can also be noted from the chart that the amount of sample finally remaining is higher than the theoretical value, which is because of the mutual linkage of TiO₂ network structure and primary bond of each monomer. This

phenomenon can improve the thermal stability of the hybrid materials effectively.²⁸⁻³¹

It can be noted from the DSC chart (Figs. 10 and 11) that, with the addition of inorganic silicon dioxide, the glass transition temperature (T_g) of each proportion increases along with the increase in inorganic TiO₂ content. The TiO₂ particles from the hydrolysis of TBOT decrease the free volume of the hybrids and makes the T_g increase. Details of each sample glass transition temperature are shown in Table IV, in which each hybrid mixture has one glass transition temperature, without any phase separation phenomenon created.^{6,7} It can be noted from the ta-

TABLE III
The Pencil Hardness of the Organic/Inorganic Hybrid Materials

Code no.	Hardness
10Ti110	H
30Ti110	2H
50Ti110	3H
70Ti110	3H
90Ti110	4H
10Si111	H
30Si111	2H
50Si111	4H
70Si111	5H
90Si111	5H

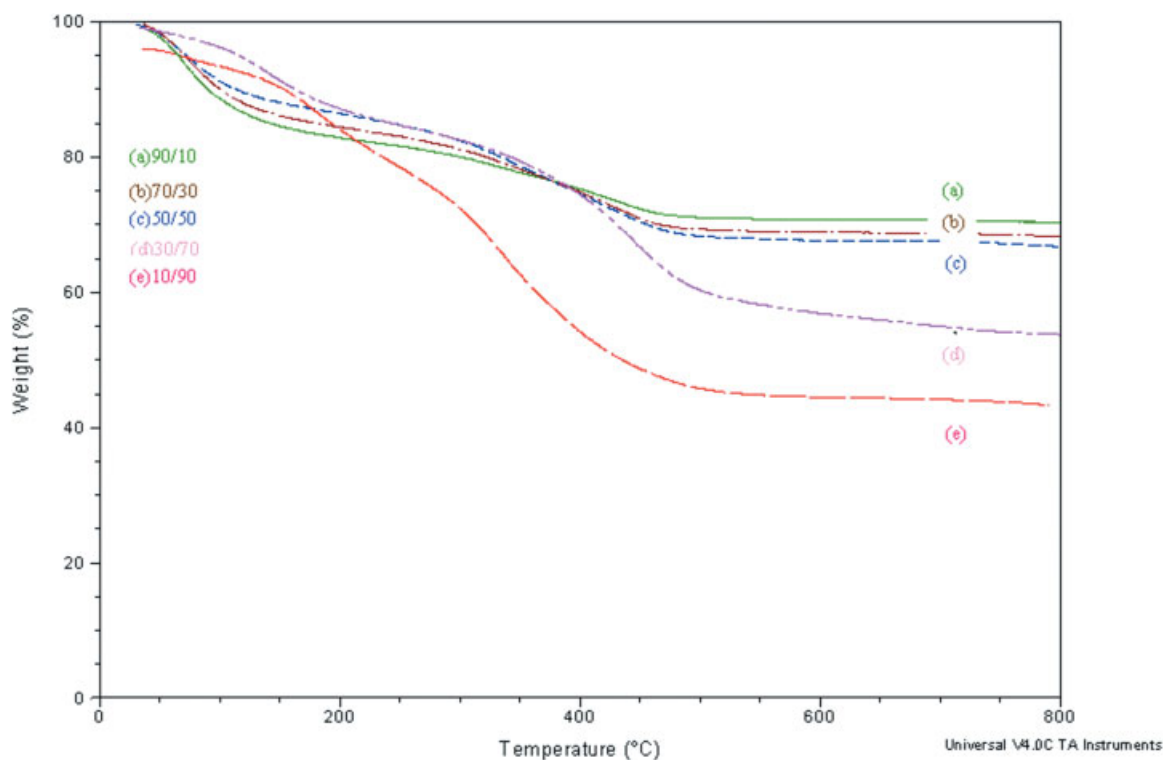


Figure 8 The TGA curves of the titanium dioxide mixed with two monomer series of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

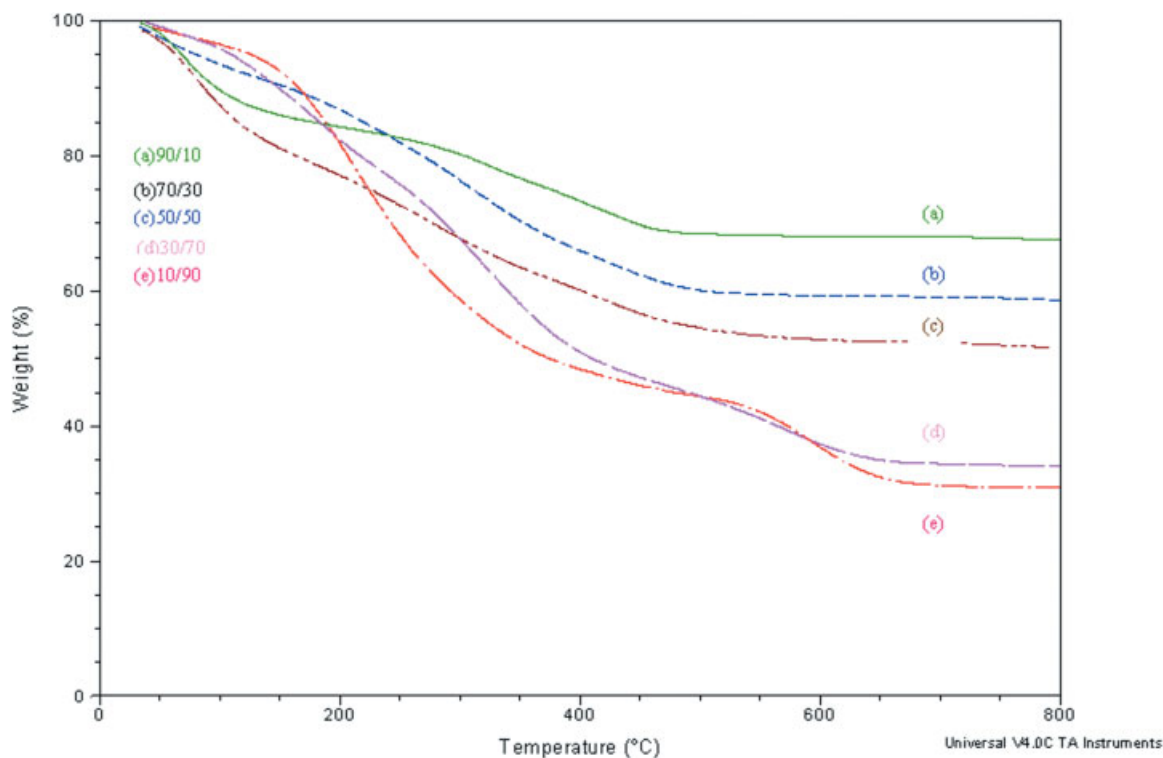


Figure 9 TGA curves of the titanium dioxide mixed with three monomer series of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

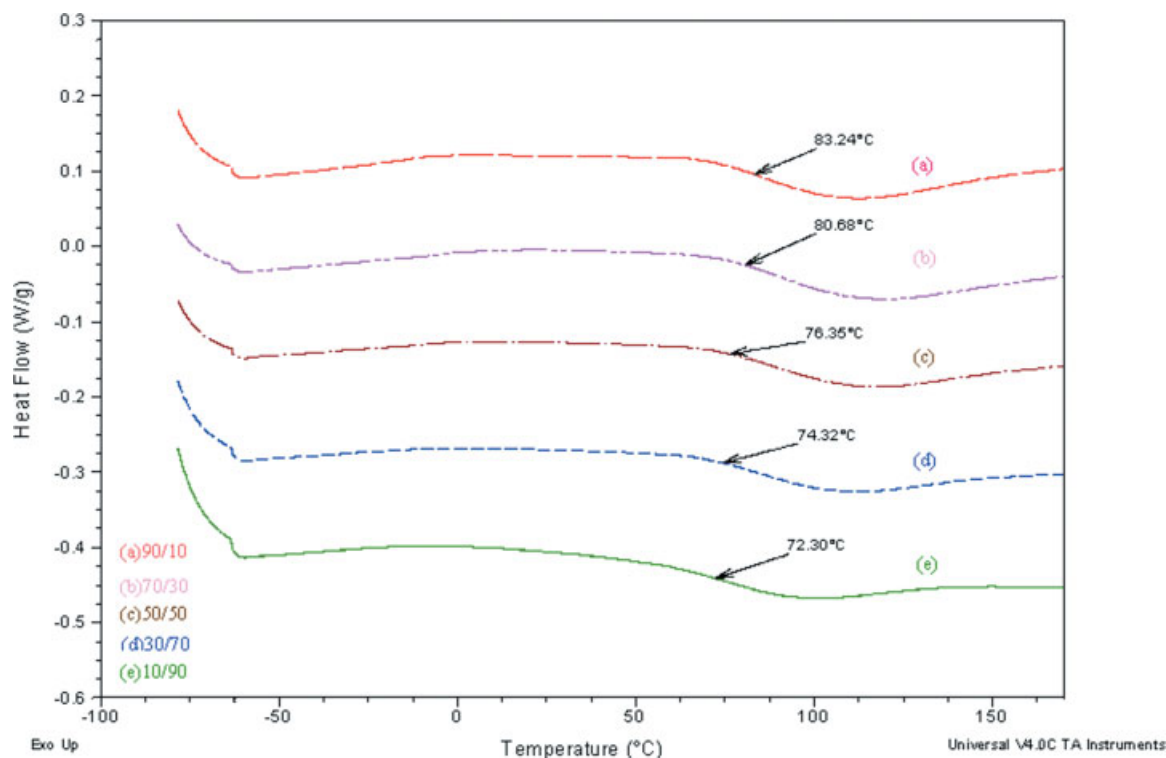


Figure 10 The DSC curves of the titanium dioxide mixed with two monomer series of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

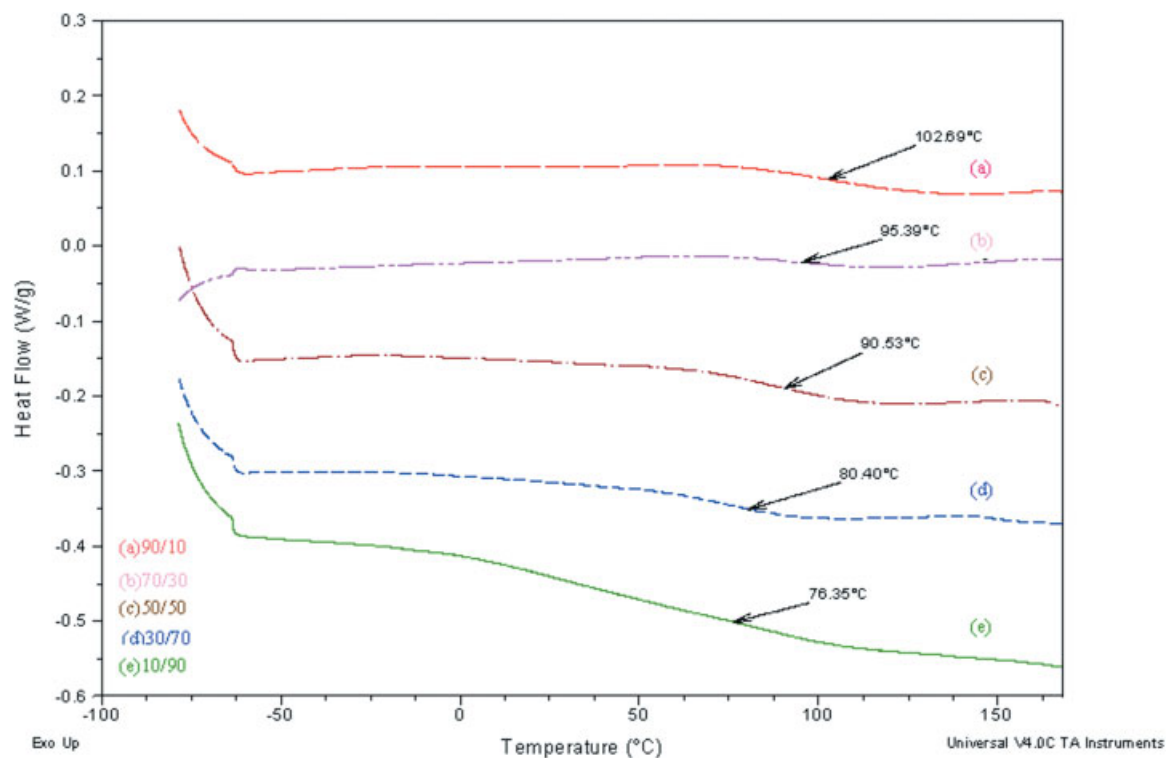


Figure 11 The DSC curves of the titanium dioxide mixed with three monomer series of inorganic/organic hybrid materials. (a) 90/10, (b) 70/30, (c) 50/50, (d) 30/70, and (e) 10/90. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
The T_g of the Organic/Inorganic Hybrid Materials

Code no.	T_g (°C)
10Ti110	60.95
30Ti110	71.56
50Ti110	73.51
70Ti110	80.40
90Ti110	93.37
90Si111	100.25
10Si111	68.24
30Si111	72.30
50Si111	76.75
70Si111	88.10

ble that the compatibility of organic/inorganic high refractive index TiO_2 hybrid mixture is good.

CONCLUSIONS

This experiment uses one of the hybrid mixtures from the two kinds of series, adding TEGDMA. The purpose is to provide higher concentration double bond, to form covalent bonds in the organic group, which will form the condition of organic network structure. Based on the above-mentioned results, it can be noted that with the addition of a crosslinking agent, TEGDMA, the absorption peak of C=C after light assembly has disappeared, proving that C=C bond has created reaction.

The pencil hardness test also proves that the addition of crosslinking agent, TEGDMA, has caused the elevation of the mechanical properties of the inorganic/organic hybrid material. In the UV/vis spectra, it can be noted that with the addition of a crosslinking agent, the refractive index has a slight upward trend; the transparency rate of thin film is still close to 90%, which conforms to the demand for optical elements with high refractive index. In terms of thermal stability, the final sample shows remnants higher than theoretical value, and this is due to the mutual linkage of TiO_2 network structure and primary bond of each monomer. It can be noted from the DSC curves that the T_g of inorganic/organic high refractive index TiO_2 hybrid mixture has upward trend along with the increase of inorganic content. The TiO_2 particles from the hydrolysis of TBOT decrease the free volume of the hybrids and makes the T_g increase. Therefore, it can be seen from these two phenomena that the thermal stability of sample has elevated and improved. From the experimental data, it can be concluded that the inorganic/organic high refractive index hybrid materials produced in this experiment has good mechanical properties, good optical and thermal stability properties.

The next future work

This research work in the future is to study high refractive index of other materials and design a antireflection (AR) multilayers for optic-device by high/low refractive index hybrid materials casting.

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