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Effect of nano-BaTiO₃ on thermal, mechanical, and electrical properties of HDDA/TPA photopolymer prepared by a digital light processor RP machine

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Abstract: The acrylate-based photopolymer consists of tetra-functional polyester acrylate (TPA), and hexanediol diacrylate (HDDA) has been successfully composited with nano barium titanate (BaTiO₃) and completely cured via a digital light processor RP machine. The degradation temperature, tensile strength, hardness, resistivity, and dielectric constant of samples were characterized by Thermo Gravimetric Analyzer Hi-Res TGA2950, Universal Tensile Machine JIA701, Hardness Shore D tester, Fluke 117 multimeter, and Agilent B1500A Semiconductor Device Analyzer, respectively. The morphology changes of the samples were also investigated using the JEOL JSM-6390LV scanning electron microscopy (SEM). The results show that the improvement of degradation temperature is not obvious. Furthermore, the modulus elasticity, hardness, and dielectric constant increase as the filler loading increases up to 2 phr, but the resistivity is vice versa. Interestingly, there is an inverse correlation between dielectric constant and resistivity of photopolymer/BaTiO₃ nanocomposite.

Keywords: dielectric constant; nanocomposite; photopolymer.

1 Introduction

Many researchers have been intensively developing photopolymer/inorganic nanocomposites for many appli-

cations especially in rapid prototyping systems [1–4]. A photopolymer/inorganic nanocomposite product manufactured by forming a prototype from a liquid precursor into a solid part has some advantages compared to the traditional one such as via melt-intercalation or common solvent mixing, which releases a large amount of volatile organic compounds (VOC) and produces an un-cross-linked polymer. Besides, photo-initiated polymerization inherently is ultra-rapid in nature and has temperature-independent reactions, spatial and temporal control of initiation, and it is also environmentally friendly [5].

Photopolymer/clay nanocomposites have been developed by Fawn et al. [5] and Decker et al. [6] based on acrylate (radically initiated photopolymer) and epoxy (cationic initiated photopolymer) systems. These nanocomposites show some improvements in both thermal and mechanical properties without any significant change in the photopolymerization rate in comparison to the pristine polymer. In our previous researches [1–3], we used TPA (tetrafunctional polyacrylate) mixed with HDDA (hexanediol diacrylate) as a matrix and a small amount of nano silica, nano clay, and carbon black as the fillers. The liquid composites were cured from liquid to solid by a digital light processor RP machine through a layer-by-layer process to form the desired prototypes. The tensile strength and hardness of HDDA-TPA/inorganic (silica, nano clay, and carbon black) nanocomposites increased approximately by 50% to 60% compared to the pristine HDDA-TPA. These fillers have successfully improved the feasibility of the HDDA/TPA photopolymer to be applied in the rapid prototyping system to manufacture the prototype products.

Other common applications of acrylate-based polymer are coating, electronic insulating, and packaging, which need considering the dielectric properties. By compositing with inorganic materials into acrylate-based polymer, it will have other possible potential applications such as film substrates and embedded dielectric materials in microelectronics. These applications usually involve heat and mechanical contact such as scratch, stress, or bending during the assembly process. Therefore, the considerations that should be taken into account are not only

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the electrical properties including dielectric constant and loss but also thermal and mechanical properties, especially degradation temperature, hardness, tensile, and impact strength.

Recently, extensive research efforts have been given to better understand and control properties of polymeric composite systems with nano-size metal-oxide inclusions. Improvements in the dielectric breakdown strength and significant change in dielectric dispersion of matrix polymers have been reported when nanometer size has been embedded. Barium titanate (BT) is one of the common dielectric inorganic ceramic materials that have been widely used in dielectric components. It is also well-known to be used as ferroelectric and piezoelectric materials. Tuncer et al. [7] presented a simple binary mixture system composed of polyvinyl alcohol (PVA) with titanium dioxide (TiO₂) and barium titanate (BaTiO₃) for cryogenic applications. Their results indicated the similar effect of both fillers in the enhancement of dielectric constant up to 220% compared to the neat PVA. They also reported the enhancement of dielectric breakdown strength up to 70% at 0.01 failure probability value, while dielectric losses have no significant decreases compared to the neat PVA.

In this research, we further investigate the electrical properties of photopolymer/BaTiO₃ nanocomposite including its dielectric constant and its dielectric loss and resistivity as well as its morphology changes and mechanical properties as the effect of BaTiO₃ filler loading in order to make it feasible to be applied in related applications.

2 Materials and methods

The reagents used, the preparation steps, and the experimental items are described as follows.

2.1 Reagents

1. Tetra function polyester acrylate (TPA, manufacturer: Henkel, type: photomer 5430, molecular formula: C₁₁H₁₃O).
2. 1,6-Hexanediol di-acrylate (HDDA, manufacturer: Henkel, type: photomer 4017, molecular formula: C₁₂H₁₈O₄).
3. Nano-barium titanate (IV) (manufacturer: Sigma-Aldrich Co., cubic crystalline phase nanopowder, size <100 nm, BET >99% trace metals basis).

4. Photo initiator (manufacturer: Ciba, type: IRGACURE 784, molecular formula: C₂₉H₁₇TiF₃N₂).

2.2 Materials preparation

Tetra function polyester acrylate (TPA) and 1,6-hexanediol di-acrylate (HDDA) were mixed with a ratio of 50:50 for about 30 min at 1000 rpm. After the BaTiO₃ filler was added, they were re-stirred for about 24 h at 1000 rpm. The liquid photopolymer/BaTiO₃ nanocomposite was cured into a solid part layer by layer with 100 μm of layer thickness by using a digital light rapid prototyping (DLRP) Machine. The DLRP machine is a computer-controlled machine designed to adjust several curing process parameters such as an area of light (masking), timing, and depth of penetration of digital light exposed into the liquid precursor (liquid photopolymer/BaTiO₃ nanocomposite) to cure the precursor into a solid part/prototype as schematically described on the previous study [1, 2]. A few percent of photo initiator was added to catalyze the photo-curing reaction when introduced under visible light to form the solid part of the photopolymer/BaTiO₃ nanocomposite. The formulations of the photopolymer/BaTiO₃ nanocomposite are listed in Table 1.

2.3 Tests

The mechanical properties such as tensile strength and hardness were measured and analyzed using a Universal Tensile Machine JIA701 and Shore D Type Durometer Hardness Tester, respectively. The thermal stability was analyzed using a Thermo Gravimetric Analyzer Hi-Res TGA2950. The morphology was observed using a scanning electron microscopy (SEM) using JEOL JSM-6390LV at 5 kV. The dielectric constant and its dielectric loss were measured using a B1500A Semiconductor Device Analyzer at 1 MHz and -5 to 5 V, while resistivity was measured using a Fluke 117 multimeter.

Table 1: Formulation of photopolymer/BaTiO₃ nanocomposite.

Sample	TPA/HDDA (phr)	Photoinitiator (phr)	BaTiO ₃ (phr)
B0	100	1.5	0
B1	100	1.5	1
B2	100	1.5	2
B3	100	1.5	3
B4	100	1.5	4
B5	100	1.5	5

3 Results and discussion

3.1 Degradation temperature analysis

In the previous study [1–3], we observed that there was a significant increment of about 60% or even greater in the degradation temperature of the photopolymer/inorganic nanocomposite by adding about 2 phr of clay, silica, and carbon black. The increment of temperature degradation is caused by compositing effects, where the inorganic fillers are well bonded within the photopolymer chain during the photo-polymerization process. But interestingly, those processes only occurred when the filler loading was under 2 phr incorporated with the disperse agent in proportional ratio of about 1:1. But, in this study, when the filler was substituted by BaTiO₃ 1–5 phr, the increment of degradation temperature of the photopolymer/BaTiO₃ nanocomposite was not obvious as shown in Figure 1A and B.

Figure 1: (A) TGA curve and (B) degradation temperature as a function of filler loading of photopolymer/BaTiO₃ nanocomposite.

However, the maximum value of degradation temperature can be reached by adding a BaTiO₃ filler at 2 phr. Compared to our previous results, the maximum degradation temperature of the photopolymer/BaTiO₃ nanocomposite is about 405°C. It was about 28°C lower than that of the photopolymer/clay nanocomposite, which has a degradation temperature of about 433°C [2]. However, it was about 70°C higher than that of the photopolymer/CB nanocomposite and photopolymer/SiO₂ nanocomposite, which have a degradation temperature of about 335°C [1, 3].

3.2 Morphology analysis

The results show that the sample without fillers (Figure 2A) has the smoothest morphology. However, the sample with 1 phr of BaTiO₃ nanoparticle displays a rough morphology. The morphology becomes rougher with a BaTiO₃ loading of up to 5 phr. The rough morphology resulted from the agglomeration of BaTiO₃ particles within the photopolymer matrix during the curing process, which was caused by the agglomeration tendency of the BaTiO₃ fillers in the photopolymer matrix due to the hydrophilic nature of the BaTiO₃ particles. The excess BaTiO₃ induces an extreme agglomeration within the photopolymer, which is shown in Figure 3. That is why some researchers suggested the *ex situ* modification of the BaTiO₃ with appropriate surfactant such as phenol to inhibit extreme agglomeration of BaTiO₃ within the polymer matrix [4].

3.3 Mechanical properties

Generally, the addition of inorganic filler materials into a polymer matrix will increase its hardness. In our previous researches [1–3], the hardness of the photopolymer was increased significantly by adding a small amount of SiO₂, carbon black, and clay together with a dispersant agent in an appropriate ratio. In this research, it was consistent with the previous results that the maximum hardness was achieved by the sample with 2 phr of BaTiO₃. But, compared to the sample with a clay filler, the sample with a BaTiO₃ filler has lower hardness value as shown in Figure 4. This indicates that the bounding tendencies of the clay filler within the photopolymer matrix (possibly intercalated, exfoliated, or flocculated as reported by Fawn et al. [5]) is stronger than that of the BaTiO₃ filler.

Figure 5 shows the effect of filler loading on the tensile strength and modulus elasticity of a photopolymer/BaTiO₃ nanocomposite. Generally, there are no significant improvements on the tensile strength and elastic

Figure 2: The morphology change become rougher as observed on SEM images of photopolymer/BaTiO₃ nanocomposite. (A) 0 phr, (B) 1 phr, (C) 2 phr, (D) 3 phr, (E) 4 phr, (F) 5 phr.

Figure 3: The extreme agglomeration tendency of nano BaTiO₃ observed on SEM image from tensile sample with 5 phr filler loading.

Figure 4: Hardness as a function of filler loading.

Figure 5: Tensile strength and modulus elasticity as a function of filler loading.

modulus of the samples with BaTiO₃ and clay fillers. But, compared to the sample with clay filler, the elastic modulus of the sample with BaTiO₃ is higher. It means that the sample with the BaTiO₃ filler is more stiff than that of the sample with the clay filler. The stiffness of the sample with the BaTiO₃ filler may be caused by the formation of agglomeration of the BaTiO₃ filler within the photopolymer matrix as shown in Figure 3. It is quite different compared to our previous result [2] that indicates the sample with clay loading, which possibly forms flocculated, intercalated, or exfoliated clay structure within photopolymer and makes the composite more elastic when subjected to tensile test.

3.4 Permittivity and resistivity

Permittivity and resistivity are crucial properties embedded within the materials related to the applications especially on the interconnection in nanoelectronic as a substrate. Figure 6 shows the dielectric constant as a function of filler loading at 1 MHz and at room temperature. The pristine photopolymer reported in this paper has permittivity of about 2.02. After composited with nano clay in several compositions, there are no significant improvements on its permittivity. Only, a maximum 1.16 of the improvement in its permittivity can be achieved by adding nano clay. This small improvement is probably caused by the possible arrangement of the clay particles within the photopolymer, which contributes to the increase in the polarizability of the photopolymer moieties that are induced by electric field. This hypothesis was more obvious after adding a photopolymer with a high polarizable dielectric ceramic material BaTiO₃ in the

Figure 6: Dielectric constant and dielectric loss at 1 MHz as a function of filler loading.

same composition. The improvement of its permittivity increased up to 1400% with a maximum of about 29.479 compared to the pristine photopolymer that had only 2.02.

Another dramatic improvement is associated with dielectric losses. Pure barium titanate normally will show the high loss about 10% up to 20% of the value of the dielectric constant. Wei et al. [8] reported that the dielectric loss of BaTiO₃ can be reduced down to 7% after composited with a small amount of Co₂O and PbTiO. However, by compositing with a photopolymer as shown in Figure 6, the decrement in the dielectric loss can be achieved below 0.05 from the maximum dielectric constant of about 29.5 or below 0.2% of the dielectric loss.

The following equation is a simple common approach of the compositing method proposed by Barber et al. [9] that was used by Lichtenecker to predict the effective dielectric constant of polymer composite system.

$$\epsilon_{\text{eff}} = \phi_1 \epsilon_1 + \phi_2 \epsilon_2 \quad (1)$$

where the subscripts 1 and 2 represent the photopolymer and the BT phase, respectively, and ϕ is the volume fraction of the constituents. Equation 1 explicitly shows the increment of the effective dielectric constant by increasing the volume fraction of the BT fillers as the effect of compositing because the dielectric constant of BT is much higher than that of the photopolymer. It was also confirmed by many related studies [4, 9–11].

Another model used to predict the effective dielectric constants is based on the mean field theory.

$$\epsilon_{\text{eff}} = \epsilon_1 \frac{\epsilon_2 + 2\epsilon_1 - 2(1-\phi_1)(\epsilon_1 - \epsilon_2)}{\epsilon_2 + 2\epsilon_1 + (1-\phi_1)(\epsilon_1 - \epsilon_2)} \quad (2)$$

Equation 2, well known as the Maxwell equation, is based on a mean field approximation of a single spherical inclusion surrounded by a continuous matrix of the polymer [9]. Thus, the Maxwell's equation is strictly valid only as the filler fraction goes to zero, i.e. infinite dilution. Another mean field theory, known as the Bruggeman model, treats the binary mixture as being composed of repeated units of cells composed of the matrix phase with spherical inclusions in the center [9]. By modifying equation 2, it can also be expressed (so-called binary mixture approach) as follows:

$$\phi_1 \left(\frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}} \right) + \phi_2 \left(\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}} \right) = 0 \quad (3)$$

However, our study tends to follow the simple approach as expressed in equation (1) only if the content of the filler loading is below 3 phr as shown in Figure 7.

Figure 7 is the plot of both theoretical and experimental data of the dielectric constant as a function of filler loading. Figure 7 shows that the sample with nano BT fillers below 3 phr has a trend curve that is close to the Lichtenecker/Bruggmann model. In other words, for the photopolymer/BT nanocomposite, the Lichtenecker/Bruggmann model is only valid for fillers below 3 phr.

Figure 8 shows a beautiful correlation between resistivity and dielectric constant as a function of filler loading. The dielectric constant increases by increasing the filler loading up to 2 phr. But, more than 2 phr, the dielectric constant remains constant. The filler loading also gives the same effect to its resistivity but *vice versa*.

Figure 7: Dielectric constant trend as a function of filler loading.

Figure 8: Inverse correlation between resistivity and dielectric constant as a function of filler loading.

The correlation of the dielectric constant and the resistivity comes from the flowing of a charge carrier within materials, which can be electrons or ions, that were caused by applying an electric field on it. If an electric field is applied across the materials, the electrons will naturally flow proportion to the strength of the electric field, thus:

$$J_c = \sigma_s E \quad (4)$$

where σ_s is a constant proportionality, and it is called “conductivity.”

On the other hand, when an external electric field is applied, the dipoles align with the field. This action causes a term to be added to the electric flux density that has the same vector direction as the applied field as described mathematically as:

$$D = \varepsilon_0 E + \varepsilon_0 \chi_e E \quad (5)$$

where χ_e is known as the electric susceptibility and serves as a proportionality constant between the electric field and the portion of the electric flux density caused by the presence of the dielectric. It can be rewritten as

$$D = \varepsilon_0 (1 + \chi_e) E \quad (6)$$

or

$$D = \varepsilon_0 \varepsilon_r E \quad (7)$$

where ε_r is known as the relative permittivity of the medium. The quantity of $\varepsilon_0 \varepsilon_r$ is usually expressed as ε . Therefore, equation (7) can be rewritten as

$$D = \varepsilon E \quad (8)$$

By substituting equation (4) to equation (8), we can get the correlation of the dielectric constant and conductivity as:

Figure 9: Numerical simulation of dielectric constant as a function of volume resistivity.

$$\varepsilon \cdot J = \sigma_s D \quad (9)$$

Because the conductivity is inversely proportional to resistivity, it gives an inverse correlation between resistivity and dielectric constant as shown in Figure 9.

Figure 9 shows the numerical simulation plot of the dielectric constant as a function of resistivity. It implies that the resistivity decreases with increasing dielectric constant.

Those correlations have been proved mathematically by Ristic et al. [12] by observing the dielectric constant and resistivity of silicon at 300 K, which is consistent with our results plotted in Figure 9.

By using curve fitting for the sample that contains the nano-BT fillers of maximum 2 phr, we can get

$$\varepsilon(\rho) = 466.22 \rho^{-2.77} \quad (10)$$

where ρ is the volume resistivity in $\times 10^9 \Omega\text{-cm}$.

However, the curve is only fitted on the data that contains not more than 2 phr of nano-BT filler loading. It indicates that the correlation between the dielectric constant and resistivity based on equation (10) is only valid for a maximum of 2 phr of BaTiO₃ filler loading.

4 Conclusions

The effect of nano-BaTiO₃ on the mechanical and electrical properties of HDDA/TPA photo-cured polymer prepared by a digital light processor RP machine was studied. The morphology of the photopolymer becomes rough by increasing the BaTiO₃ filler loading. The maximum value of the degradation temperature, modulus elasticity, and hardness was obtained by adding a BaTiO₃ filler loading of 2 phr. It indicates that the optimum filler loading is 2 phr. On the other hand, the dielectric constant of the sample increases by increasing the BaTiO₃ filler loading, but resistivity tends to decrease *vice versa*. Those results make the photopolymer/BaTiO₃ nanocomposite as being considered as a candidate for electronic material applications such as a substrate with embedded capacitors.

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