Mechanical and Dielectric Properties of Polyhedral Oligomeric Silsesquioxanes Modified Graphene Oxide/Polyimide Nanocomposites

Chen-Chi M. Ma*, Sheng-Chi Lin, Jeng-An Wang,
Wei-Hao Liao, Sheng-Tsung Hsiao, Yu-Sheng Wang and Shin-Ming Li

Department of Chemical Engineering, National Tsing Hua University,
101, Section 2, Kuang-Fu Road, Hsin-chu 30013, Taiwan, R.O.C
E-mail: ccma@che.nthu.edu.tw

Excerpt from ISBN 978-3-00-053387-7

Keywords: graphene oxide, octa(aminophenyl) POSS, mechanical properties, dielectric properties

Abstract

An effective method is proposed to prepare octa(aminophenyl) silsesquioxane (OAPS) functionalized graphene oxide (GO) reinforced polyimide (PI) composites with a low dielectric constant and ultrastrong mechanical properties. The amine-functionalized surface of OAPS-GO is a versatile starting platform for in situ polymerization, which promotes the uniform dispersion of OAPS-GO in the PI matrix. Compared with GO/PI composites, the strong interfacial interaction between OAPS-GO and the PI matrix through covalent bonds facilitates a load transfer from the PI matrix to the OAPS-GO. The OAPS-GO/PI composite film with 3.0 wt % OAPS-GO exhibited 11.2-folds increase in tensile strength, and 10.4-folds enhancement in tensile modulus compared with neat PI. The dielectric constant (Dk) decreased with the increasing content of 2D porous OAPS-GO, and a Dk value of 1.9 was achieved.

1. RESULT AND DISCUSSION

1.1. MECHANICAL PROPERTIES OF THE OAPS-GO/PI COMPOSITE FILMS

The reinforcing effects of the GO and OAPS-GO on the tensile properties of the PI composites are summarized in Figure 1 and Table 1. The tensile modulus of GO/PI composites increased from 2.20 to 3.28 GPa (approximately a 49% increase over neat PI film), and the tensile strength increased from 88.5 to 168.6 MPa (approximately a 91% increase over neat PI film) when the GO content increased from 0 to 1.0 wt %. Moreover, as the GO content increased from 1.0 to 3.0 and 5.0 wt %, the tensile modulus of the GO/PI composites increased to 6.25 and 7.29 GPa, respectively, but a decreasing trend was observed on the tensile strength of the GO/PI composites. This decreasing trend of the tensile strength was attributed to the filled GO reaching critical content,[1] and the distance between any two GO sheets being extremely short, causing van der Waals forces to become significant. Consequently, the GO agglomerated and restacked together (as observed in the SEM images of Figure 2c, d), which reduced the effective contact area between the GO surface and the PI polymer matrix. As the OAPS-GO loading increased from 0 to 3.0 wt %, the tensile modulus and tensile strength increased from 2.20 GPa and 88.5 MPa to 22.8 GPa and 986.8 MPa, respectively.

Compared with neat PI films, the OAPS-GO/PI composite film with only 3.0 wt % OAPS-GO exhibited a dramatic increase in tensile modulus (approximately 10.4 fold). In addition, 3.0 wt % OAPS-GO/PI possessed a substantial improvement in tensile strength (approximately 11.2 fold increase over neat PI film), revealing that OAPS-GO possessed a high reinforcing efficiency for promoting the load transfer from the polymer to OAPSGO. This high-efficiency reinforcement might be attributable to the well-dispersed OAPS-GO in the polymeric matrix, as well as to the formation of strong interfaces between OAPS-GO and the PI matrix (as indicated in the SEM images of Figure 2e, f). Consequently, two reasons were proposed for the superior tensile properties of the OAPS-GO/PI composite films compared with GO/PI composites: (1) the grafted OAPS onto the GO surface can obtain a large interlayer spacing, preventing the restacking of the GO sheets, and (2) the OAPS-GO surface can provide abundant amine-functional groups for grafting PAA through the in situ polymerization.

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The grafted PI molecular chains on the OAPS-GO surface through covalent bonding caused a larger reinforcing zone and higher reinforcing efficiency than those of pristine GO in the PI matrix, which provides a high ability for transferring the stress from the PI polymeric matrix to OAPS-GO (as shown in Figure 9). Furthermore, as the OAPS-GO content increased from 3.0 to 5.0 wt %, the reinforcing efficiency of OAPS-GO decreased slightly, and a similar trend was observed for the tensile modulus of the OAPS-GO/PI composite films. This indicates that the filler reached a critical content,[1] and the OAPS-GO sheets may agglomerate or restack, reducing the contact and reactive surface between OAPS-GO and PI, and the reinforcing efficiency of the mechanical properties was decreased. Therefore, an appropriate filler content of OAPS-GO can optimize the mechanical properties of the material. In summary, the OAPS-GO/PI composite films, which exhibited excellent tensile properties, suggest that OAPS-GO is an effective and versatile starting platform for preparing the PI composite films by using in situ polymerization.

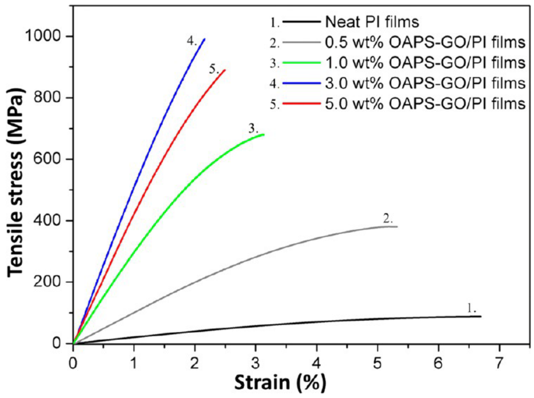

Figure 1. Stress−strain curves of neat PI films and OAPS-GO/PI films with various amounts of OAPS-GO.

Table 1. Mechanical Properties of Neat PI, GO/PI, and OAPS-GO/PI composites

sample	tensile modulus (GPa)	tensile strength (MPa)	elongation at break (%)
neat PI	2.20 ± 0.07	88.5 ± 6.1	6.69 ± 0.32
0.5 wt % GO/PI	3.28 ± 0.12	135.1 ± 9.5	5.52 ± 0.35
1.0 wt % GO/PI	4.63 ± 0.26	168.6 ± 10.4	4.82 ± 0.28
3.0 wt % GO/PI	6.25 ± 0.31	152.3 ± 12.6	4.55 ± 0.25
5.0 wt % GO/PI	7.29 ± 0.38	146.7 ± 10.2	4.28 ± 0.68
0.5 wt % OAPS-GO/PI	9.25 ± 0.56	378.6 ± 15.8	5.31 ± 0.42
1.0 wt % OAPS-GO/PI	15.6 ± 0.85	679.5 ± 36.1	3.13 ± 0.59
3.0 wt % OAPS-GO/PI	22.8 ± 0.92	986.8 ± 50.6	2.16 ± 0.55
5.0 wt % OAPS-GO/PI	21.6 ± 0.98	890.7 ± 58.2	2.49 ± 0.68

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1.2. DIELECTRIC PROPERTIES OF THE OAPS-GO/PI COMPOSITE FILMS.

The GO surface possesses a high density of oxygen containing functional groups, which is an electrically insulating material.[3] These carbon−oxygen bonds were formed on the GO surface, and the sp^2-hybridized carbon atoms in graphite were transferred to the sp^3-hybridized carbon atoms in GO, causing the π-electrons were confined due to the incomplete conjugation. Because the D_k of air is approximately 1.0,[4] the nanoporous OAPS was grafted onto the GO surfaces to form OAPS-GO to achieve more insulating than GO. In this study, the insulating OAPS-GO sheets were introduced as interlayers in the PI matrix, restricting electron mobility in the OAPS-GO/ PI composite.

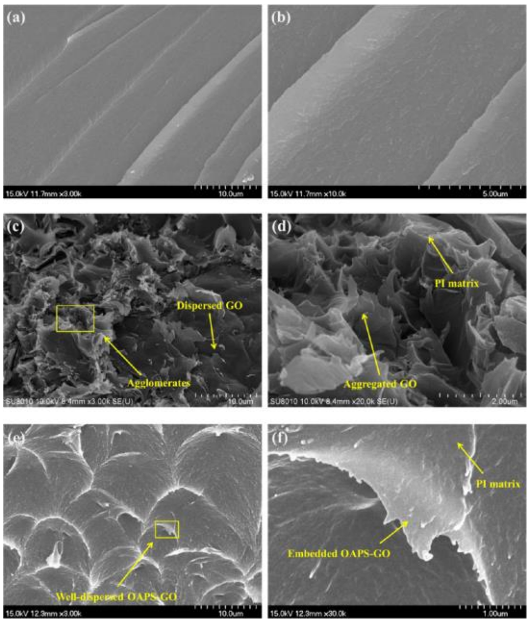

Figure 2. SEM images of fractured surface of (a) neat PI (×3k), (b) neat PI (×10k), (c) 3.0 wt % GO/PI film (×3k) and, (d) 3.0 wt % GO/PI film (×20k), (e) 3.0 wt % OAPS-GO/PI film (×10k), and, (f) 3.0 wt % OAPS-GO/PI film (×30k).

Figure 3 presents the dielectric spectra of the neat PI films, the GO/PI composite films and the OAPS-GO/PI composite films, with the increasing of filler content (from 0.5 to 5.0 wt %), over a frequency range of 0.01 to 1 GHz. The neat PI films exhibited dielectric constant of approximately 3.3. The addition of GO and OAPS-GO content, and the GO/PI films and OAPS-GO/PI films possessed significantly lower D_k value than that of neat PI. It is worth noting that the change in D_k is not proportional to the content of GO nor OAPS-GO, and relatively large change occurs at the GO or OAPS-GO content below 1.0 wt %. Because the 2D layered structure and insulation of GO or OAPS-GO in the PI matrix may prevent the partial PI molecular chains from exhibiting the polarization effect[5] as the GO or OAPS-GO filler content is below 1.0 wt %, and the dielectric constants of the composites are considerably reduced.

However, the other part of the PI molecular chains in these composites still encounters strong polarization effect. The quantity required for the GO or OAPS-GO sheets to effectively restrain the polarization effect in the PI molecular chains gradually trended toward saturation as the filler content surpassed 1.0 wt %. Therefore, the rate of D_k reduction in the composites at high filler contents is less than that of the composites at low filler contents; this phenomenon has also been observed in previous studies.[6]

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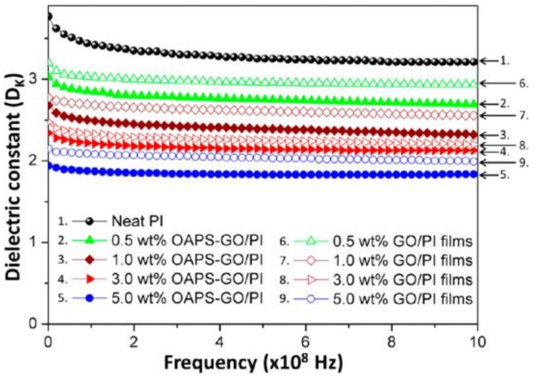

Figure 3. Dielectric constant as a function of frequency for neat PI films, OAPS-GO/PI films, and OAPS-GO/PI films.

The dielectric constant of 5.0 wt % GO/PI films is approximately 2.1 (line 9 in Figure 3), and 5.0 wt % OAPS-GO/PI films achieved a D_k value of approximately 1.9 (line 5 in Figure 3). Compared with the GO/PI composite films, the OAPS-GO/PI composite films exhibited a greater reduction of the dielectric constant, indicating that the cage-structural OAPS with a nanoporous core (D_k of air is approximately 1.0.)[4] was grafted onto the GO surface, which could provide higher insulating properties than the pristine GO sheets could. This paper reports that the OAPS-GO/PI composite films with low D_k values can be fabricated through in situ polymerization, which had achieved the current requirement for ILD materials.

2. CONCLUSIONS

This study demonstrates an effective method for preparing OAPS-GO/PI composite films with ultrastrong mechanical properties and a low dielectric constant. The 3.0 wt % OAPS-GO/PI composite films, prepared by in situ polymerization, exhibited approximately 10.4-folds increase in tensile modulus, and 11.2-folds increase in tensile strength. Furthermore, the bulk dielectric constant decreased from 3.3 of the neat PI film to 1.9 of the 5.0 wt % OAPS-GO/PI composite films. The performance of the OAPS-GO/PI composite films was substantially superior to that of the GO/PI composite films. Consequently, a 2D porous OAPS-GO was designed as a novel nanofiller to reinforce the polymeric matrix and provide an effective method for fabricating OAPS-GO/PI composite films with low dielectric constants and excellent mechanical properties for a wide range of applications.

Acknowledgments

This work was supported by the Ministry of Science and Technology, Taipei, Taiwan, under Contracts 103-2221-E-007-001-(103) and 103-2221-E-007-130-(103). Boost Program from Low Carbon Energy Research Center of National Tsing Hua University is gratefully acknowledged.

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