We have successfully prepared ultraviolet (UV) curable organic/inorganic hybrid nanocomposites with good thermal stability, moderate adhesion strength, and excellent barrier capability. In order to improve the gas blocking properties, the metal alloy (Invar) has been blended with lab-made organic/inorganic hybrid nanocomposites, dramatically not only raising the gas resistance but also reducing the shrinkage after UV curing. Moreover, we have also applied lab-made nanocomposite IV for the encapsulation of organic solar cells. The experimental results reveal that introduction of nanocomposite IV can effectively block the penetration of moisture as well as oxygen in the air into the devices and consequently promote the lifetime of organic solar cells.

1. Introduction

Organic/inorganic hybrid nanocomposites, which are composed of polymer matrices, fillers, and initiators, have attracted lots of attention for several decades because they can resist the penetration of oxygen as well as moisture in the atmosphere and are used in the preservation of food as well as beverages [1]. Pure polymers, such as acrylics and epoxy resins, have been extensively applied for the polymer matrices of organic/inorganic hybrid nanocomposites due to their low cost, high processing facility, and moderate toughness.

Acrylics resins [2] are well-known polymeric materials since they exhibit quick curing speed, high structural strength, and excellent processing convenience. Their fast curing performances are suitable for some electronic applications, such as the bonding of magnets into speaker assemblies, and others with high assembly line speed. Furthermore, they can be cured with heat or ultraviolet (UV) irradiation [3,4] by the addition of thermal initiators or photoinitiators, respectively. UV curable acrylics resins have shorter curing time, weaker structure strength, and higher contraction than thermal curable ones. Although acrylics resins are good candidates for polymer matrices of organic/inorganic hybrid nanocomposites, they exhibit low viscosity. This extremely restricts their practicability.

Epoxy resins [5] are also famous polymeric materials because of their chemical modifiability, high transparency, good thermal stability, and moderate viscosity. In recent years, they have been used in electronic, mechanic, and biological industrials since the oxirane groups of epoxy resins are active to various functional groups such as alcohol, thiol, anhydride, amine, etc., facilitating the curing reaction. They can be cured with heat or UV irradiation [6] by the addition of curing agents or photoinitiators, respectively. Compared with UV curable epoxy resins, thermal curable ones have longer curing duration and the color stain takes place while they are cured at high temperature. Despite the epoxy resins have many merits as the polymer matrices of organic/inorganic hybrid nanocomposites; they exhibit low curing speed and high brittleness after curing.

In order to increase the gas barrier performances of polymer matrices, some researchers have recently added fillers (e.g. silica, metal oxide, clay, etc.) into them to enhance their gas barrier capability [7–11]. Nonetheless, the resistance of gas for polymer matrices/fillers was not satisfied. Therefore, we have tried to blend metal alloys with polymer matrices/nano-fillers to further reduce the gas penetration.
As described above, acrylics resins possess low viscosity and high contraction after curing. However, epoxy resins exhibit moderate viscosity and low contraction after curing. In addition, epoxy resins have long curing time and high brittleness after curing. Oppositely, acrylics resins possess high curing speed and low brittleness after curing. Thus, we have chosen these two complementary materials as the polymer matrices to modulate the physical, chemical, and mechanical properties.

In this paper, we have firstly synthesized thermal curing acrylics resins with appropriate viscosity by addition of thermal initiators. Then epoxy resins and photoinitiators have been added into the acrylics resins and eventually the polymer matrices can be prepared. Since UV curable acrylics resins have weaker structure strength and thermal curable epoxy resins are prone to coloration, we have manipulated acrylics and epoxy resin to be thermal and UV curable, respectively. Finally, we have blended the nano-filler (silica) as well as the metal alloy (Invar) with the polymer matrices to accomplish the manufacture of lab-made organic/inorganic hybrid nanocomposites. After UV irradiation, lab-made organic/inorganic hybrid nanocomposites can be cured and bonded with the glass. The experimental results manifest that addition of Invar into polymer matrices/silica effectively increases the gas barrier capa-

![Fig. 1. Chemical structures of the resin monomers, initiators, and materials for organic solar cells.](image)

![Fig. 2. Structures of lab-made organic solar cells. (a) ITO glass/PEDOT (30 nm)/P3HT:PCDM (50 nm)/LiF (10 nm)/Al (80 nm); (b) ITO glass/PEDOT (30 nm)/P3HT:PCDM (50 nm)/LiF (10 nm)/Al (80 nm)/encapsulating adhesive (100 μm).](image)
we have also utilized lab-made organic/inorganic hybrid nanocomposites for the encapsulation of organic solar cells, demonstrating they can effectively resist the invasion of moisture and oxygen in the air into the devices. Consequently, the lifetime of organic solar cells with their package is much longer than that without package.

2. Experimental

2.1. Materials

All of resin monomers, initiators, materials for organic solar cells, solvents, and fillers (silica: 30–100 nm) used in the experiment (Fig. 1) were purchased from Aldrich Co. and used without further purification. 1,6-Hexanediol diacrylate and 3,4-epoxycyclohexane carb-oxylode were the monomers for acrylics and epoxy resins, respectively. Benzoyl peroxide and triaryl sulfonium hexafluorotiminate were utilized as thermal initiators and photoinitiators, respectively. Propylene glycol monomethyl ether acetate (PGMEA) was the solvent. The metal alloy (Invar) purchased from Goodfellow Co. was iron/nickel composite (64/36 = wt%/wt%, size = 100 nm).

Table 1

Physical properties of lab-made organic/inorganic hybrid nanocomposites

<table>
<thead>
<tr>
<th>Material</th>
<th>T_d (°C)</th>
<th>Adhesion strength (Kgf/cm²)</th>
<th>Gas penetration (%)</th>
<th>Electrical conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocomposite I</td>
<td>345</td>
<td>117.5</td>
<td>10.71</td>
<td>$1.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>Nanocomposite II</td>
<td>328</td>
<td>107.4</td>
<td>8.17</td>
<td>$2.3 \times 10^{-10}$</td>
</tr>
<tr>
<td>Nanocomposite III</td>
<td>340</td>
<td>90.7</td>
<td>7.34</td>
<td>$4.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>Nanocomposite IV</td>
<td>335</td>
<td>87.3</td>
<td>5.12</td>
<td>$6.8 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Fig. 3. TGA of lab-made organic/inorganic hybrid nanocomposites in air.

Fig. 4. TEM of nanocomposites (a) I, (b) II, (c) III, and (d) IV.
2.2. Preparation of lab-made organic/inorganic hybrid nanocomposites

1,6-Hexanediol diacrylate (10 g), benzoyl peroxide (0.1 g), and PGMEA (100 mL) were heated at 100 °C for 3 h. After blended with 3,4-epoxycyclohexene carboxylode (10 g) and triaryl sulfonium hexafluoroantimonate (0.1 g), the acrylics/epoxy resins (polymer matrices) were obtained. Then we added silica (50 wt%) and Invar (0–15 wt%) into the polymer matrices and lab-made organic/inorganic hybrid nanocomposites were finally prepared (nanocomposite I: with 0 wt% Invar; nanocomposite II: with 5 wt% Invar; nanocomposite III: with 10 wt% Invar; nanocomposite IV: with 15 wt% Invar). After coated on the glass with spin-coating technique and irradiated by UV for 1 min, lab-made organic/inorganic hybrid nanocomposites could be cured and bonded with the glass.

2.3. Fabrication of organic solar cells

We ultrasonically washed the ITO glass (5 Ω/e) with the acetone, methanol, and de-ionized water for 5 min, dried it with a stream of nitrogen as well as the oven, and treated it with O₂ plasma for 90 s. Polyethylene dioxythiophene (PEDOT) was then dissolved in water (3 wt%), filtered with a 0.2 μm filter, and deposited onto the ITO glass by spin-coating (stage I: 1000 rpm for 20 s; stage II: 3000 rpm for 30 s). Afterwards, the P3HT powder (molecular weight = 87,000) was ground together with PCBM (purity = 98%) to form P3HT/PCBM mixture (weight ratio = 1/1). Then the P3HT/PCBM mixture was dissolved in dichloromethane (2 wt%), filtered with a 0.2 μm filter, and deposited onto the PEDOT layer by spin-coating (stage I: 1000 rpm for 20 s; stage II: 2000 rpm for 30 s). Finally, we deposited LiF and Al electrode onto the P3HT/PCBM layer by vacuum evaporation as shown in Fig. 2(a).

The encapsulation of lab-made organic solar cells was executed with spin-coating of nanocomposite IV on the Al electrode (stage I: 500 rpm for 10 s; stage II: 1500 rpm for 20 s) and under UV illumination for 10 s (Fig. 2(b)). The thickness of encapsulating adhesive was 100 μm.

2.4. Instruments

Thermogravimetric analysis (TGA), gas penetration, transmission electron micrograph (TEM), and electrical conductivity were measured by a JHS-100, an Illinois-8501, a Philips/Tecnai F20, and an Everbeing SR-4, respectively. Thermomechanic analysis (TMA), adhesion strength, and film thickness were recorded on a Seiko SSC 5000, a micro-computer universal testing machine (Hung Ta Co.) with the standard test method (ASTM D1002) and a surface profiler (TENCOR P-10), respectively. The current–voltage (I–V) curves for organic solar cells were measured in the air by an instrument (Keithley 238), whose accuracy can reach picoampere, under illumination of white light from a 300 W halogen lamp (Saturn Co.) whose intensity was recorded on a radiometer (IL-1700). The UV lamp utilized for UV curing was an Entela UVP 100 W.

3. Results and discussion

3.1. Polymer matrices

Although 1,6-hexanediol diacrylate exhibits good mechanic properties, low brittleness after curing, and short curing time, it possesses weak thermal stability, low viscosity, and high contraction after UV curing.
3.3. Thermal mechanic properties and adhesion strength of organic/inorganic hybrid nanocomposites

As shown in Table 1 and Fig. 5, addition of Invar not only enhances the gas barrier capability but also reduces the shrinkage. Furthermore, the dimension change in planar direction decreases with the increase of Invar as shown in Fig. 5. Nevertheless, the adhesion strength drops with the raising of Invar owing to the poor adhesion energy of metal with the glass.

3.4. Encapsulation of organic solar cells

Although silicon-based solar cells have been found to exhibit good efficiency for the conversion of sunlight into electrical energy, their cost is very high. In recent years, organic solar cells have become alternative candidates for photoelectric conversion because of low cost and high processability. Nevertheless, the lifetime of organic solar cells has been an essential hindrance for the commercialization since oxygen and moisture in the air erode the organic materials and metal electrodes of devices, dramatically dropping the lifetime. In addition, most researches focus on the improvement of the efficiency for solar cells but the studies about the promotion of lifetime are less reported.

As shown in Fig. 6(a) and Table 2, lab-made organic solar cell without encapsulation exhibits the photoelectric conversion properties initially and its efficiency reaches to be 0.42%. While the actuating time proceeds, nonetheless, the photoelectric conversion capability gradually decays because the moisture and oxygen in the atmosphere invade into the device, causing the corrosion of organic materials and metal electrode. After actuated for 48 h, the efficiency merely remains to be 0.016% (decay ratio = 96.2%).

In order to improve the lifetime of organic solar cells, we have tried to applied nanocomposite IV for the package of the devices. With the encapsulation of nanocomposite IV, as manifested in the Fig. 6(b) and Table 2, the decay ratio sharply decreases and can be only 13.0% and 37.0% when the actuating time are 15 and 48 h, respectively. The result proves that nanocomposite IV is capable of resisting the penetration of oxygen as well as moisture in the air into the device, effectively prolonging the lifetime of organic solar cells. Furthermore, the similar result can also be observed in the case of commercial encapsulating adhesive (EPO-TEK 301, Epoxy Technology Co.) as shown in Fig. 6(c) and Table 2. Compared with the photoelectric conversion properties of organic solar cells with EPO-TEK 301, the decay ratio of the device with the package of nanocomposite IV is lower, revealing that the nanocomposite IV exhibits better gas barrier capability than EPO-TEK 301.

4. Conclusions

In conclusion, novel UV curable organic/inorganic hybrid nanocomposites (acylicresins/epoxyresins/silica/Invar) with excellent gas barrier performance, moderate adhesion strength, low
shrinkage, good thermal resistance, and fast curing speed have been successfully synthesized and applied for the encapsulation of organic solar cells. We have found that lab-made nanocomposites effectively impede the penetration of moisture and oxygen in the atmosphere into the device and consequently prolong the lifetime. In the near future, we will further explore their mechanical, chemical, and physical properties and utilize them for the package of other electronic devices (e.g. LEDs, semiconductor chips, LCDs, and so on).

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References