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Barrier properties and structure of liquid crystalline epoxy and its nanocomposites

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ABSTRACT

There is ever increasing demand for a suitable sealant material to protect electronic devices, in particular, different displays. We present a new approach to generate a liquid processible material that possesses excellent barrier properties and flexibility that can be used for electronic encapsulation. The liquid processable material is based on liquid crystalline (LC) epoxy diglycidyl ether of 4, 4′-dihydroxy-α-methylstilbene (DGE-DHAMS or EDHAMS) and its nanocomposite comprising organo-modified montmorillonite clay. The best-achieved water vapor transmission rate is 4.5 g-mil/m^2-day at ambient pressure, which is more than 20 times better than that of a conventional bisphenol A epoxy. The improved barrier performance comes from the reduction in the water diffusivity. The diffusivity in the liquid crystalline epoxy is 1.25×10^{-9} cm^2/s, one order of magnitude lower than that of bisphenol A epoxy. The addition of 1 vol% of organoclay further reduces the diffusivity by 2 times. The cavity size of the free volume of the liquid crystalline epoxy is much smaller than that of conventional bisphenol A epoxy as measured by positron annihilation lifetime spectroscopy, suggesting that the improved barrier property originates from this reduced free volume cavity size. The free volume cavity size of the film with an addition of 1 vol% of an organically modified montmorillonite clay is similar to that of the liquid crystalline epoxy. We hypothesize that the additional barrier performance improvement by the nanoclay is due to its effect on the liquid crystalline phase morphology (reduced LC phase domain sizes) or the tortuosity effect of the high aspect ratio particles. The material also has excellent adhesion, optical transparency, and thermal stability.

1. Introduction

Electronic devices are typically sensitive to moisture and oxygen. [1] Edge sealant is usually applied to the frame of a device to protect it and prolong its lifetime. Using an OLED display as an example, Fig. 1 shows advantages and disadvantages of different encapsulation technologies. [2–4] Desired properties of edge sealant materials include high barrier properties, hight flexiblility, sufficient adhesion and are easy to process. In addition to the need for better water barrier properties, current sealants often lack sufficient flexibility and crack when the device is bent. It is therefore important to develop new materials that improve on these deficiences. The existing sealants for rigid middle size displays are mainly glass frits, which need higher processing temperature and are not flexible, and therefore are not suitable for flexible or large size devices. Another commonly used sealant material, epoxides, can provide the flexibility, but do not have sufficient barrier properties. For instance, according to Table 1 bisphenol A based epoxy (BPA) has a reported water vapor transmission rate of about 100 g-mil/m^2-day-atm [5], which is about ten times worse than poly(-vinylidene chloride) [6], a well-known polymer with excellent water barrier properties. Epoxides are important materials in constructing electronic devices, and extensive work was carried out to further improve the mechanical and electric properties of epoxides including the use of bifillers of core-shell SiO_2@MWNTs and montmorillonite, polymer modified graphene oxide, and layer-by-layer carbon nanotube grafting to carbon fibers. [7–9] This work aims to improve the overall performance of sealants by developing liquid processable materials that have improved water barrier properties and flexibility.

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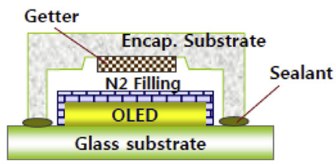
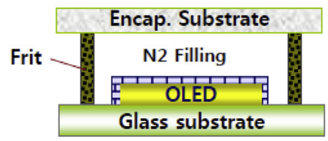
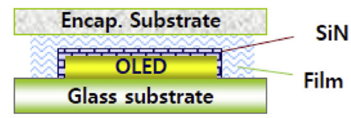
Type	Metal/Glass Lid Type	Frit Seal	Face Seal
Structure			
Concept	Organic Sealing	Frit Sealing	Film Face Sealing
Emission	Bottom Emission	Top/Bottom Emission	Top/Bottom Emission
Size	Small Size Panel (<15 inch)	Middle Size Panel (~20 inch)	Large Size Panel (>40 inch)
Advantages	Simple Process	Simple Process	High Shock Resistance Stable Gap
Disadvantages	Thicker Panel	Low Shock Resistance	

Fig. 1. Advantages and disadvantages of different encapsulation technologies.

The water vapor transmission, or permeability, is the product of solubility and diffusivity. For polymers, the high diffusivity due to free volume is the leading cause of higher permeability compared to other classes of material such as metal or ceramics. Previous work suggests that thermoplastic liquid crystalline polymers can efficiently reduce the free volume and improve barrier properties. [10] However, thermal processing is not suitable for electronics encapsulation. We, therefore, hypothesized that a thermosetting liquid crystalline polymer could minimize free volume and improve barrier properties. Further, we were interested in the incorporation of inorganic platelike fillers and how they might further enhance barrier properties through a tortuous path. Nanoclay has been a filler of interest due to its unique shape and very high aspect ratio. [11] There have been numerous studies demonstrating that the addition of nanoclay to epoxies and other polymers can improve barrier properties. [5,12–15] Some work was carried out on the study of the thermal plastic liquid crystalline polymer and its nanoclay composites. [16–18] However, there is insufficient research in exploring the combination of liquid crystalline epoxy and the addition of nanoclay [19] and no reported study on its effect on the barrier performance. In this work, we would like to contribute our work on the liquid crystalline epoxy containing stilbene and its nanocomposite containing montmorillonite clay to understand their barrier properties.

Table 1
Water vapor transmission rate of different polymers.

	Water Vapor Transmission Rate (g*mil/m^2*day*atm)
PVDC (Saran) [6]	20
PE [20]	189
PET [20]	20–600
BPA epoxy [5,13]	100

2. Experimental

2.1. Materials

The diglycidyl ether of 4, 4′-dihydroxy-α-methylstilbene (DGE-DHAMS) was synthesized in-house; [21] sulphanilamide (SAA, analytical grade) and diaminodiphenylsulfone (DDS, analytical grade) were purchased from Sinopharm Chemical Co. Organic clay (cloisite I 30A) was acquired from South Clay. All chemicals were used as received. The chemical structures are shown in Scheme 1.

2.2. Equipment

Table 2 summarizes the equipments used in the film fabrication.

2.3. Barrier film preparation

2.3.1. EDHAMS film (ES) fabrication

A release agent was coated on the glass plate (100*150 mm). Copper tape with different thicknesses were bonded on the glass plate. EDHAMS (10 g) and sulphanilamide (2.42 g) or diaminodiphenylsulfone (1.82 g) were melted at 150 °C and then mixed together at this temperature. The mixture was poured onto the surface of the heated glass plate (the surface temperature: ~150 °C). On this glass plate, another glass plate was layered slowly to avoid any air bubbles. The two plates were pressed slightly. It was then cured for 2 h at 150 °C in the oven after completing all operations. According to the liquid crystalline phase time-temperature-transformation (LCPTTT) diagrams [22], a liquid crystalline phase would form under this curing conditions.

2.3.2. EDHAMS/clay film (ESC) fabrication (hybrid films)

A release agent was coated on the glass plate (100*150 mm). Copper tape with different thicknesses were bonded on the glass