Composition Optimization of Transparent Glass-fabric Reinforced Siloxane Hybrid (GFRHybrimer) Films for Thermally Stable Flexible Display Substrate Film

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Abstract

Composition of siloxane hybrid material (hybrimer) was optimized to fabricate glass-fabric reinforced siloxane hybrid (GFRHybrimer) with high transparency and thermal stability. Refractive index of the hybrimer was precisely controlled by changing the phenyl precursor and adding a low refractive index crosslinker monomer. By measuring the thermal stability of GFRHybrimer films fabricated with a refractive index matched using cycloaliphatic epoxy oligosiloxane (CAEO), we obtained an optimal CAEO composition. The optimized GFRHybrimer film showed a high transparency (90%) and good thermal stability (1% weight loss temperature of 365 ^{o}C). Also, the fabricated GFRhybrimer film showed a smooth surface (R_{rms} = 0.265 nm), low coefficient of thermal expansion (~14 ppm/^{o}C), and high elastic modulus (7 GPa).

Author Keywords

Glass-fabric reinforced plastic; Siloxane hybrids; Flexible display substrate; Thermal stability; Optical transparency.

1. Introduction

Recently, flexible displays have been remarked on as a key trend of future displays. Compared to conventional displays, flexible displays not only offer a variety of new design possibilities but also offer strengths in such areas as lightness and durability [1]. To change the rigid display to the flexible one, the glass substrate should change to flexible material [2]. Many candidate substrates, such as metal foils [3], thin glass [4], and polymer films [5] have been suggested for flexible substrate materials. Among those candidates, plastic films are considered as a promising material due to their flexible, transparent, lightweight, and rugged characteristics [6].

The critical characteristics that limit polymer films as substrate materials are the thermal resistance and the dimensional stability [7]. In detail, most polymer films show low thermal decomposition temperature and high coefficient of thermal expansion (CTE) values. From the perspective of dimensional stability, furthermore, glass transition behavior around its glass transition temperature (i.e., an abrupt change in CTE around that temperature) is another factor that limits the process temperature of polymer film substrates. Among the synthetic plastic films, polyimide (PI) film satisfies the above criteria of flexible substrate materials [8]. However, the inherent yellowness and high birefringence of the PI film limit its usage as a substrate film in many applications such as flexible transparent displays [9]. Therefore, many types of research on colorless polyimide (CPI) film have been done to overcome these negative characteristics of PI film [10]. However, the thermal stability of CPI film is significantly lower than that of PI film. Also, high cost of the precursors and usage of large amounts of solvents can be the disadvantages of the CPI films [11].

Therefore, a transparent, low cost, solvent-free, glass-fabric reinforced siloxane hybrid (GFRHybrimer) film with high thermal stability and low CTE value has been proposed as another candidate transparent flexible substrate material to replace CPI film [12, 13]. Among the many characteristics of GFRHybrimer, the optical transparency and thermal stability are greatly affected by the siloxane hybrid (hybrimer) matrix. Therefore, optimization of the composition of the hybrimer is an important part of the fabrication process of a GFRHybrimer with great transparency and a good thermal property. In this work, we demonstrate an optimization process for GFRHybrimer by controlling the composition of the hybrimer matrix.

2. Results and Discussion

GFRHybrimer film is a type of glass-fabric-reinforced plastic (GFRP) that uses a hybrimer as its matrix material. A common feature of GFRP films is excellent dimensional stability (including low CTE and high modulus) due to reinforcement effect the effect of the glass-fabric [14]. However, most of the properties of GFRP, including optical transparency and thermal stability, are greatly dependent on the matrix material. Therefore, optimization of the hybrimer matrix is important for the fabrication of a high performance GFRHybrimer film with high optical transparency and thermal stability.

First, we focused on fabricating GFRHybrimer film with the hightest transparency. Figure 1, shows the structure of the GFRHybrimer films. When light goes through the GFRHybrimer, the light passes through the hybrimer matrix and the glass-fabric. If the refractive index of the hybrimer matrix is different from the refractive index of the glass-fabric, light is scattered at hybrimer/glass interfaces [9, 15]. On the other hand, if the refractive index of the hybrimer matrix is matched with the one of the glass-fabric, refraction or reflection at the interface does not occur, making film transparent. Therefore, refractive index matching between the glass-fabric and the hybrimer matrix is very important in the fabrication of a GFRHybrimer film with high transparency.

By changing the amount of phenyl groups and low refractive crosslinker, the refractive index of cycloepoxy siloxane hybrid (CEH) was tuned. Lowering the refractive index of CEH matrix was done by lowering the phenyl amount or adding more low refractve index crosslinker and vice versa when raising the refractive index. Through the two methods of refractive index tuning, we fabricated CAEO resin with different percentages of phenyl and different amounts of crosslinkers. Figure 2(a) shows the refractive indices (at 632.8 nm), as variation of phenyl groups and amount of crosslinkers. To find the optimal refractive index of the CEH resin, GFRHybrimer films were fabricated with CEH matrices with different refractive indices. Figure 2(b) shows the transparency of the GFRHybrimer film as a function of the refractive index of the CEH matrix. From the experimental

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results, we found the optimal refractive index of CEH matrix that shows highest transparency. Figure 2(b) provides a digital photograph of the transparent GFRHybrimer film fabricated with a refractive index matched CEH matrix. This refractive index matched transparent GFRHybrimer showed a high transparency of 90%

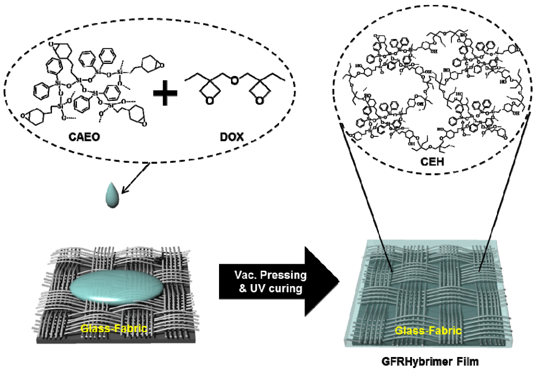

Figure 1. Schematic illustration of fabrication process of GFRHybrimer film.

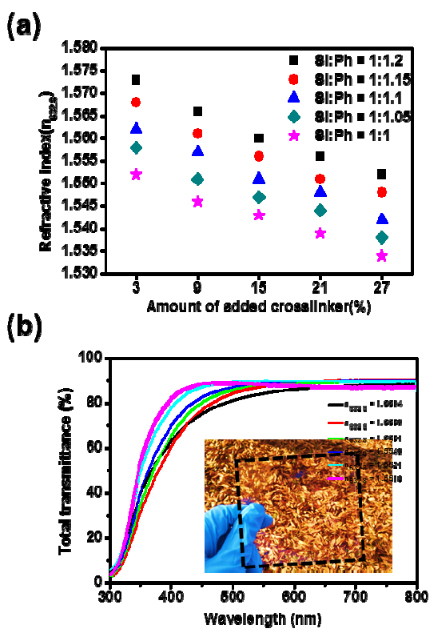

Figure 2. (a) Refractive indices (at 632.8 nm) of CEH bulks with different Ph to Si molar ratios as function of the amount of crosslinker added. (b) UV-Vis spectra of GFRHybrimer films with various refractive indices and digital photograph of the transparent GFRHybrimer film

After optimizing the refractive index of CEH matrices, thermal stability depending on phenyl and crosslinker amount was analyzed. By comparing the thermal stability values of the various refractive index matched CEH materials with different Ph to Si molar ratios, the optimal composition of the hybrimer matrix was decided. Figure 3(a) displays the TGA profile of the GFRHybrimer films fabricated with refractive index matched CAEO resins. In the low temperature region, degradation of volatile molecules, such as low molecular weight oligosiloxanes or unreacted silanes, is a major issue affecting the thermal stability of the GFRHybrimer film. In the high temperature region where the linkage between crosslinker and CAEO becomes unstable, causing the epoxide linkage to decompose. Therefore, due to the high amount of DOX added, CEH with high phenyl content decomposes faster compared to CEH with low phenyl content at high temperature.

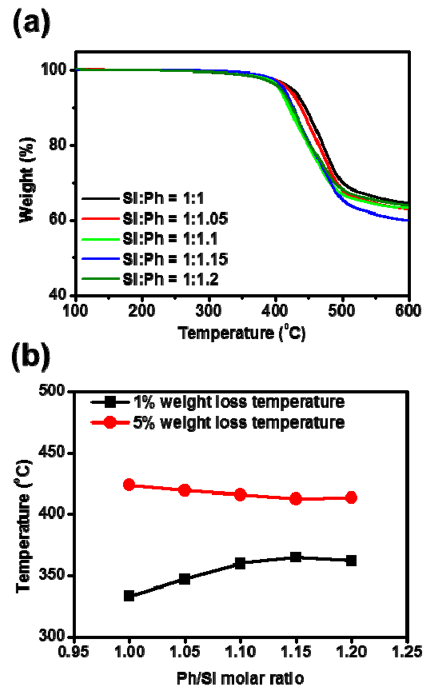

Figure 3. (a) TGA curves of GFRHybrimer films with different Ph to Si molar ratios (N_2 atmosphere, 5 ^{0}C/min.). (b) 1% and 5% weight loss temperature values of GFRHybrimer films with different Ph to Si molar ratios, derived from Figure 3(a).

Using the results of the thermal stability analysis, the composition of the hybrimer matrix was optimized. With the optimized composition of the GFRHybrimer film, the macroscopic properties of the substrate material, such as the flexibility, surface roughness, coefficient of thermal expansion (CTE), and elastic modulus, were analyzed.

Figure 4(a) shows a tilted-view cross-sectional SEM image of the GFRHybrimer film. In this image, it can be seen that the glass-fabric is well-impregnated inside the CEH matrix. To precisely verify the surface rougheness of the GFRHybrimer film, AFM analysis was performed to measure the surface topology of the film. Figure 4(b) shows the 3D AFM surface profile of the GFRHybrimer film. Common polymer films used for the substrates, such as polyethylene terephthalate (PET) and PI films, shows root-mean-square roughness (R_{rms}) values of around 0.8 nm. In comparison, the R_{rms} of the GFRHybrimer film showed a value of 0.237 nm, indicating that the GFRHybrimer film has an extremely smooth surface compared to those of other polymer films.

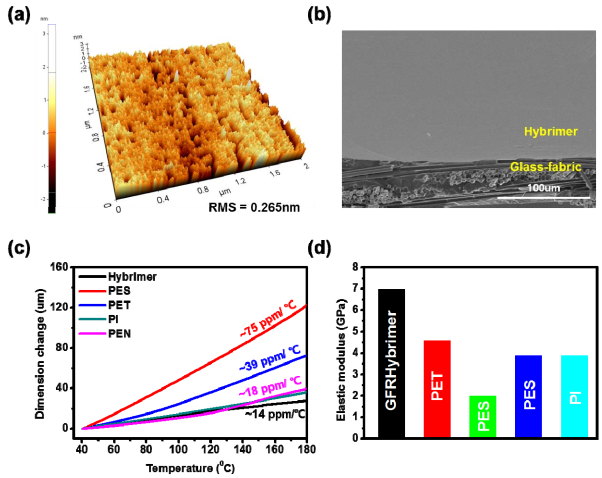

Figure 4. (a) Tilted-view cross-sectional SEM image of GFRHybrimer film. (b) 3D AFM surface profile of GFRHybrimer film. (c) TMA curves and (d) elastic moduli of the GFRHybrimer film, and of conventional polymer films, including PET, PES, PEN, and PI.

The dimensional stability of the substrate against outer stresses due to high temperature during the fabrication processes of a device is another very important issue. Thermomechanical analysis (TMA) and tensile testing were performed to check the dimensional stability of the GFRHybrimer film. Figure 4(c) shows TMA curves of the GFRHybrimer film and of conventional polymer films including PET, polyethersulfone (PES), polyethylene naphthalate (PEN), and PI. It should be noted that the CTE of the GFRHybrimer film shows a value of 14 ppm/^{o}C, which is a low value compared to those of other polymer films. The TMA results indicate that the GFRHybrimer film, in contrast to other polymer films, shows good dimensional stability in a high-temperature fabrication process. The glass-fabric impregnated by the hybrimer matrix inhibits the expansion of the film due to heat. For a similar reason, due to the reinforcement effect of the glass-fabric, the GFRHybrimer film shows a high elastic modulus compared to those of other plastic films. Figure 5(b) shows the elastic moduli of the various polymer films used as substrate materials. The results of TMA analysis and of the tensile test indicate that the GFRHybrimer film has an excellent dimensional stability compared to that of other plastic films.

3. Conclusion

To summarize, by precise refractive index tuning and thermal analysis, the composition of the CEH matrix of a GFRHybrimer film was optimized to yield the best possible transparency and thermal stability. Precise refractive index matching was performed by changing the molar ratio of Ph to Si of the CAEO resin and by adding a low refractive index crosslinker. By analyzing the thermal stability of GFRHybrimer films fabricated with various compositions, the composition of the CAEO resin that showed the highest thermal stability was determined. The characteristics of the GFRHybrimer film were then analyzed to assess films for utilization as flexible substrate materials. The optimized GFRHybrimer film showed a high transparency and good thermal stability, a smooth surface, a low coefficient of thermal expansion, and a high elastic modulus. Due to the reinforcement effect of the glass-fabric, compared to other polymer films, the GFRHybrimer film shows outstanding dimensional stability and thermal resistance.

4. Impact of Research

This research is about the method to fabricate the flexible GFRHybrimer film with excellent transparency and low CTE. We expect GFRHybrimer to be the promising candidate for flexible transparent, thermally stable substrate film for flexible display.

5. Acknowledgements

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