Highly Transparent Polymer Substrates for Flexible Displays Using Semi-Interconnected Interpenetrating Polymer Networks

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Semi-interconnected interpenetrating polymer networks (SIPNs) based on unsaturated polyurethane (UP) and different monomers, including styrene and acrylate with an UP ratio of 50 wt%, were synthesized. The resulting SIPN films exhibited excellent optical transparency in the visible range with >90% transmittance at 400 nm. The glass transition temperature ($T_g$) varied in the range of 100–135 °C depending on the unsaturated monomers introduced. They also had good flexibility compared to the conventional rigid polystyrene or polyacrylate due to the homogeneously dispersed elastic urethane moiety in the SIPNs. Below the glass transition temperature ($T_g$) of the SIPN substrates, the ITO-grown SIPN films exhibited good electrical and optical properties, showing potential as a promising substrate in flexible display applications.

Keywords: Flexible Substrate, Semi-Interconnected Interpenetrating Polymer Network (SIPN), Polyurethane, Polyacrylate, Unsaturated Polyester.

1. INTRODUCTION

With digitalization, a great deal of information is being exchanged through electronic media. Consumers are demanding more hi-quality, convenient and portable digital devices.1,2 Polymer as a substrate is a promising material for flexible displays with many advantageous characteristics including transparency, light weight flexibility and robustness. They are one of the cheapest materials and suitable for mass-production using roll-to-roll processes.

Many polymers, including polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyetherether-ketone (PEEK), polycarbonate (PC), polyethersulphone (PES), polyyarylate (PAR), polycyclic olefin (PCO) and polyimide (PI) have been studied as a substrate for flexible displays.3–9 Polystyrene and polyacrylate show very good optical transparency in the visible range and are used widely as a substitute for glass, such as transparent cases, windows, and lens, etc. However, despite these excellent optical properties, their mechanical properties, especially their pliability, are unsuitable for flexible substrates. A typical interpenetrating polymer network (IPN) consists of a multicomponent network of two or more polymers that are entangled to form physical cross-links but with no covalent bonding between the two networks.10–12 These entangled polymer chain structures strongly affect the thermal, mechanical and chemical properties of IPN. However, it is difficult to synthesize an optically transparent and completely homogeneous IPN film at high temperatures, particularly at temperatures higher than $T_g$, using conventional IPN technology due to the low miscibility between the two different polymers. Semi-interconnected interpenetrating polymer networks (SIPNs), in which the two networks are bonded to each other through chains of another polymer, improve the miscibility between different polymers.13 These bridges, which are known as intranetwork bridges, are formed by a reaction of the monomer with the sites of unsaturation present on the adjacent chains of the unsaturated polymer network, and can affect the IPN structure and properties considerably.14,15

In this study, SIPNs were synthesized based on unsaturated polyurethane (UP) with an UP ratio of 50 wt%. Indium tin oxide (ITO) was deposited on the SIPN films by radio-frequency (RF) sputtering. This paper reports the optical, physical, and thermal properties of the UP-based SIPNs as well as their feasibility as a flexible substrate.
2. EXPERIMENTAL DETAILS

2.1. Preparation of SIPN Substrates

Bisphenol A glycerolate dimethacrylate (BGDMA, Aldrich) which has two hydroxyl groups and two unsaturated methacrylates, was used to synthesize the unsaturated polyurethanes through a urethane reaction with isophorone diisocyanate (IPDI, Aldrich). Polycaprolactone triol (PCT, Aldrich) was used as a crosslinker of unsaturated polyurethane. Bisphenol A ethoxylated diacrylate (BPDA, Hannong Chemical), styrene (St, Junsei), and isobornyl methacrylate (IBMA, Aldrich) were used for radical polymerization with unsaturated polyurethane through thermal initiation of 2,2′-azobis-(2,4dimethyl-valeronitrile (AVN, Wako Chemical).

Three types of SIPNs were synthesized using three different unsaturated monomers, including styrene (St), isobornyl methacrylate (IBMA), and bisphenol A ethoxylated diacrylate (BPDA). All samples contained 50 wt% polyurethane (PU), and 50 wt% polycrylate (PA) or polystyrene (PS). BGDMA, PCT and AVN were mixed with St, IBMA, or BPDA monomers and stirred for one hour in a degassing chamber. IPDI was added dropwise to the solution and stirred again for 10 hours at approximately 35 °C in a glove box purged with nitrogen. The resulting viscous liquid mixture was then transferred to clean dry glass substrates and sandwiched between two glasses to make a 0.1 mm thick SIPN film in a 0.1 mm thick silicon rubber mold as described in Figure 1.

2.2. Deposition of ITO Thin Films onto the IPN Substrates

The ITO thin films were deposited onto SIPN films with a thickness of 0.1 mm at different temperatures ranging from room temperature to 200 °C using a typical radio frequency (13.56 MHz) planar magnetron sputtering system. The ITO target was composed of 90 wt% In2O3 and 10 wt% SnO2. The system was pumped to a base pressure of 10−7 Torr and back filled with argon to a pressure of 1.0 Pa. The sputtering power was 80 W.

3. RESULTS AND DISCUSSION

Figure 2 shows the FT-IR spectra of a mixture of the starting materials (a) and the resulting SIPN films (b–d). The strong absorption of the uncured mixture of the materials at approximately 2254 cm−1, which was assigned to the −N=C=O stretching vibration, was not observed in the resulting SIPN films, indicating that unsaturated PU networks were formed successfully through a polyurethane reaction between the isocyanates of IPDI and the hydroxyl groups of BGDMA and PCT. The C=O double bond stretching peak and C–H out-of-plane bending peak of the vinyl groups in the unsaturated monomers, which appeared weakly at approximately 1637 and 911 cm−1 in Figure 2(a), were also absent in the post-cured SIPN films, suggesting that almost all of the double bonds of the unsaturated monomers had been used in radical polymerization to create intranetworking bridges between the unsaturated PU chains.

All the SIPN films showed good toughness and pliability, as shown in the inset in Figure 3. The Young’s modulus and elongation at break of St-IPN, IBMA-IPN, and BPDA-IPN were 0.82 ± 0.2 GPa/10 ± 3%, 1.041 ± 0.3 GPa/6 ± 2%, and 1.064 ± 0.3 GPa/16 ± 3%, respectively. The BPDA-IPN film containing a robust bisphenol A moiety in the IPN main chain showed the highest mechanical properties, particularly good flexibility. Figure 3 shows the optical transmittance of the SIPNs with a thickness of 100 μm. The transmittance of St-IPN, IBMA-IPN, and BPDA-IPN at 400 nm was 89, 90 and 92%, respectively, which are comparable to that of polystyrene (PS) or poly(methyl methacrylate) (PMMA) due to their significantly short absorption edge wavelength near 300 nm as well as the absolutely low optical loss by light scattering.
at the interface between the polyurethane networks and intranetworking bridges. This indicates that the intranetworking bridge chains originating from the unsaturated monomers were dispersed homogeneously in the UP networks to completely inhibit light scattering by the heterogeneous phase of the SIPN films.

Figure 4 shows the temperature dependence of the dynamic mechanical loss tangent of the SIPNs. All the SIPNs showed a single glass transition with a sharp transition in the tan $\delta$ curve, indicating that two polymer chains including polyurethane and polyacrylate are dispersed homogeneously in the SIPN matrix. This also supports the excellent optical properties of the SIPN films, which showed >90% transmittance at 400 nm comparable to the acrylate homopolymer. The glass transition temperatures of BPDA-IPN, IBMA-IPN, and St-IPN appeared at approximately 103, 130, and 133 °C, respectively. The soft ethoxy groups of BPDA decreased the $T_g$ of the SIPN significantly despite its rigid biphenyl moiety. Compared to the $T_g$ of the homopolymers, such as polystyrene ($T_g \sim 95$ °C) and poly(isobornyl methacrylate) ($T_g \sim 110$ °C), their SIPNs had a higher $T_g$ due to the rigid structure of BGDMA and the hard segments of the PU chains. The decomposition of fully aliphatic moieties, such as the polyacrylate of the SIPNs, were observed at the lowest temperature of approximately 200 °C, followed in order by polystyrene and UP networks, which contain the thermally stable bisphenol A moiety and polycaprolactone.

Figure 5 presents the optical transmittance of the 100 nm thick ITO thin films deposited on the SIPN films at different substrate temperatures ranging from 25 and 200 °C. The absorption edges of the ITO thin films moved to a shorter wavelength with increasing substrate temperature due to the increase in density and doping effect of the ITO thin films, indicating an increase in transmittance at short wavelengths. The shift in the absorption edge, which is known as the Burstein shift, originates from the blocking of the lowest states of the conduction band by the partial filling of carriers with increasing carrier concentration above the Mott critical density of In$_2$O$_3$.5 $\delta$6 As shown in Figure 6, the average transmittance in the visible range (400–800 nm), which is generally influenced by light scattering at the grain boundaries as well as by the absorption edge of the ITO thin film, also increased with increasing substrate temperature. The average transmittance of the BPDA-IPN film, which has the lowest $T_g$ among the resulting SIPN films, began to decrease at a substrate temperature of 100 °C, dropping significantly to approximately 62% at 200 °C. This can be explained by 100 °C being close to the $T_g$ where the polymer loses its glasslike properties as a result of segmental motion of the chains. The rubber-like surfaces of the film are easily damaged by the bombardment of accelerated ITO particles, which disturbs the nucleation and growth process of the ITO thin film. The IBMA-IPN film also exhibits optical loss at a substrate temperature of approximately 200 °C close to its decomposition temperature. Interestingly, St-IPN, which has a $T_g$ at approximately 133 °C,
and a decomposition temperature at approximately 300 °C, exhibited good optical properties up to 200 °C even above its $T_g$, which was attributed to the rigid structure of polystyrene and the thermosetting properties of the network structure of SIPN.

Figure 6 shows the electrical sheet resistance of the ITO films as a function of the substrate temperature. As reported in many papers,\textsuperscript{4–6} the sheet resistance of the ITO coated on substrates was decreased as the ITO deposition temperature increased. This is a typical trend that the carrier concentrations in the ITO films became higher at higher deposition temperatures because of enhanced diffusion of tin (Sn) atoms leading to improved electron donation of Sn to In atoms at high temperatures. The sheet resistance of the ITO grown SIPN films is also affected by the thermal properties of the SIPNs used as a substrate. The sheet resistance of ITO on BPDA-IPN and IBMA-IPN showed a minima at deposition temperatures of 100 and 150 °C, respectively. However, they increased with increasing deposition temperature above 150 and 200 °C, which are close to $T_g$ and the decomposition temperature of BPDA-IPN and IBMA-IPN, respectively. On the other hand, the ITO thin film deposited on the St-IPN film showed a more stable sheet resistance up to 200 °C, whereas it also exhibits a small increase in sheet resistance at 200 °C compared to 150 °C. This shows good agreement with the optical properties of ITO deposited thin films.

The typical four strong orientations [(222), (400), (440), and (622)] in the XRD patterns of Figure 7 conformed to the polycrystalline cubic structure of ITO thin films.\textsuperscript{8} Very weak peaks, which were difficult to discriminate from the substrate peaks, were observed below 100 °C. The peak intensity increased with increasing substrate temperature to 200 °C, indicating the growth of ITO grains. The calculated average grain size (using the Scherrer formula) of the ITO thin films grown at 150 and 200 °C were 15.2 and 18.7 nm, respectively.

4. CONCLUSION

Semi-interconnected interpenetrating polymer networks (SIPNs) were synthesized based on unsaturated polyurethane (UP) that was reacted with different monomers including styrene, acrylate, and unsaturated polyester (PE) with a UP ratio of 50 wt%. The resulting SIPN films exhibited excellent optical transparency in the visible range, showing >90% transmittance at 400 nm. The glass transition temperature ($T_g$) varied from 100 to 135 °C depending on the unsaturated monomers introduced. They also showed good flexibility compared to the conventional rigid polystyrene or polycrylates due to the homogeneously dispersed elastic urethane moieties in the SIPNs. For the use of the substrate in flexible displays, an indium tin oxide (ITO) thin film was deposited on SIPN films using a radio-frequency (r.f.) planar magnetron sputtering system. Below the $T_g$ of the SIPN films, the ITO grown SIPN films showed good electrical and optical properties highlighting their potential as a substrate for flexible displays.

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References and Notes


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