Abstract - Block copolymers based on polycarbonate (PC) and polydimethylsiloxane (PDMS) have been known for over 40 years. These materials have achieved commercial success due to a favorable combination of low temperature impact, melt processibility, weathering resistance and unique surface properties. Most commercial products are opaque due to scattering by the PDMS domains dispersed in the PC matrix. By controlling synthesis conditions, optically opaque or transparent materials may result from the same combination of base monomers and both types of materials have been prepared and characterized. Lower PDMS block lengths lead to higher levels of light transmission. Opaque materials typically have siloxane domains in the 5 um region while low haze products can be achieved when domains are less than 20 nm. Small siloxane domain copolymers exhibit considerable mixing of PC into the PDMS blocks. This likely alters the refractive index of the PDMS phase and contributes to the low haze measured in these copolymers.

Introduction (Times New Roman 10, bold)
Block copolymers based on polycarbonate (PC) and polydimethylsiloxane (PDMS) were first prepared by Vaughn in the 1960s1,2. Depending on the composition of the PC-siloxane copolymer (e.g. siloxane block length and weight-% siloxane), the resulting materials will either be flexible thermoplastic elastomers (TPEs) or phase-separated rigid thermoplastics.

PC/PDMS copolymers exhibit, to a significant extent, the characteristics of a polymer blend between two essentially incompatible polymers (most notably, opacity)3,4,5,6,7. However, by controlling the synthesis conditions, optically opaque and transparent materials can be produced. Large PDMS blocks typically opacify the PC/PDMS copolymer. As block length is reduced, more transparent materials can be achieved. This paper covers some of the morphological changes that occur as PDMS domain size is reduced.

Experimental
Eugenol stopped D47 and D30 fluids were supplied by GE Silicones. Copolymers of these monomers with bisphenol A (BPA) were prepared by interfacial polycondensation methods. Recent process improvements now allow production of transparent, thermoplastic PC-siloxane copolymers suitable for a variety of injection-molding applications. The improvements involve, essentially, pre-formation of chloroformate end-group BPA-PC oligomers in the interfacial reaction prior to addition of the phenol-capped siloxane. Alternately8, the chloroformate of the siloxane can be preformed before reaction with BPA or BPA oligomers. Careful control of the molecular weight of the PC oligomers results in control of the PC block length in the final copolymer, and thus the distance between siloxane blocks. (Fig 1,2).

Results and Discussion (Times New Roman 10, bold)
Transmission Electron Microscopy (TEM) samples (100 nm) were prepared from injection molded chips on a Leica UCT ultramicrotome. Photomicrographs were obtained from a Philips CM12 TEM operated at 120 kV. Images were digitally captured by a Gatan Model 791 side mount camera. TEM photomicrographs were analyzed using Clemex Vision PE software to calculate the area fraction of siloxane domains (based upon gray scale thresholding). Small Angle X-ray Scattering studies were done on a Hecus Braun system coupled with a Kratky camera. Spectra were acquired through a slit beam x-ray, with a point approximation for calculation of various parameters.
morphology does not change drastically. However, as noted above, the inferences tend to be more qualitative than quantitative at this point with TEM. To gain more information regarding morphology, samples were analyzed via small angle x-ray scattering (SAXS).

SAXS works on the principle of scattering due to density fluctuations on extremely small scale and hence is a useful technique to understand and quantify PC/PDMS copolymer morphology. Based upon SAXS data, it is possible to calculate the siloxane domain sizes in various PC/PDMS copolymer samples. These calculations lead to a composite model for morphology.

Several interesting features arise out of the study:

(1) For both D-47 and D-30 samples, the calculated volume fraction of siloxane domains is greater than the actual loading of siloxane (5%). This strengthens the hypothesis that the siloxane domains are actually not pure PDMS, but merely siloxane rich, with some mixing of BPA-PC chains within the PDMS structure.

(2) The calculated volume fraction (and area fraction) of siloxane domains is greater in the case of D-30, 5% siloxane, as compared to D-50, 5% siloxane (before and after annealing), by as much as 50%. A rough calculation shows that the incorporation of BPA-PC chains in the D-50 samples can be roughly 30-35%, while in the D-30 samples, it can be as high as 60-65%. This fact can lead to significantly lower RI mismatch between the matrix and dispersed phase in the D-30 samples. It also explains the fact that while the siloxane domain size itself does not change drastically from the D-50 to the D-30 samples, the inter-domain spacing reduces significantly.

(3) Upon annealing, the domain size is observed to decrease slightly, likely due to diffusion of some BPA-PC chains out of the siloxane. This is also supported by the fact that the SAXS intensity peaks after annealing are sharper, indicating a stronger density mismatch between the dispersed and matrix phases.

(4) There is good correlation between the SAXS and TEM results (within the bounds of experimental error, especially in TEM image analysis).

Figure 1 – Schematic of siloxane block arrangement in opaque and clear PC/PDMS copolymers. The square blocks represent siloxane, while the circular blocks represent BPA-PC units.

Figure 2 – Typical morphology in (a) opaque and (b) PC/PDMS copolymers with a 5% loading of siloxane as observed through TEM studies.

Conclusion

PC/PDMS copolymers have been prepared and characterized. TEM and SAXS analysis show that volume percentage of PDMS domains greatly exceeds that expected based on the formulated composition. Significant mixing of PC in the PDMS domains is strongly indicated. Such mixing leads to lower haze than would be predicted from domain size data alone.

References