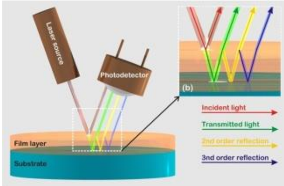
ThetaMetrisis APPLICATION NOTE #013

Simultaneous Real-time monitoring of film thickness and refractive index during thermal processing



Goal: The determination of glass transition temperature of polymeric films through the real time monitoring of thickness and refractive index of the film during thermal processing.

Means & Methods: An FR-Thermal VIS/NIR configured to operate in the 360-1000nm spectral range is used. The hot plate integrated on the tool, is controlled either manually or through the FR-Monitor software. In the present case the thickness and the refractive index (Cauchy model) of the film are monitored during the heating at a constant rate. The polymers investigated were poly(iso-butyl methacrylate) (PiBMA), poly(n-propyl methacrylate) (PPMA) and poly(ethyl methacrylate) (PEMA) and their films are spin coated on silicon wafers. Prior to the measurements the samples have been Post Apply Baked at 145°C for 15min.

Results: The heating rate is a 2-3°C/min and the polymeric film thickness and the refractive index are monitored at 50 measurements / min and both parameters are plotted vs. temperature, figs. 1a-c. Clearly the polymeric film thickness increase linearly with temperature at two temperature regimes. The intersect point of the extrapolated linear sections is defined as the grass transition temperature (Tg) of the polymer[1]. The Tg values for these poly(alkyl methacrylate) films were found to be in agreement with the literature[2,3].
The thickness increase rate is in good agreement with the reported values in the literature of thermal expansion coefficient at each polymer's "rubbery phase" i.e. at temperature values higher than Tg and in the same order of magnitude with the reported values in the "glassy phase" [4].

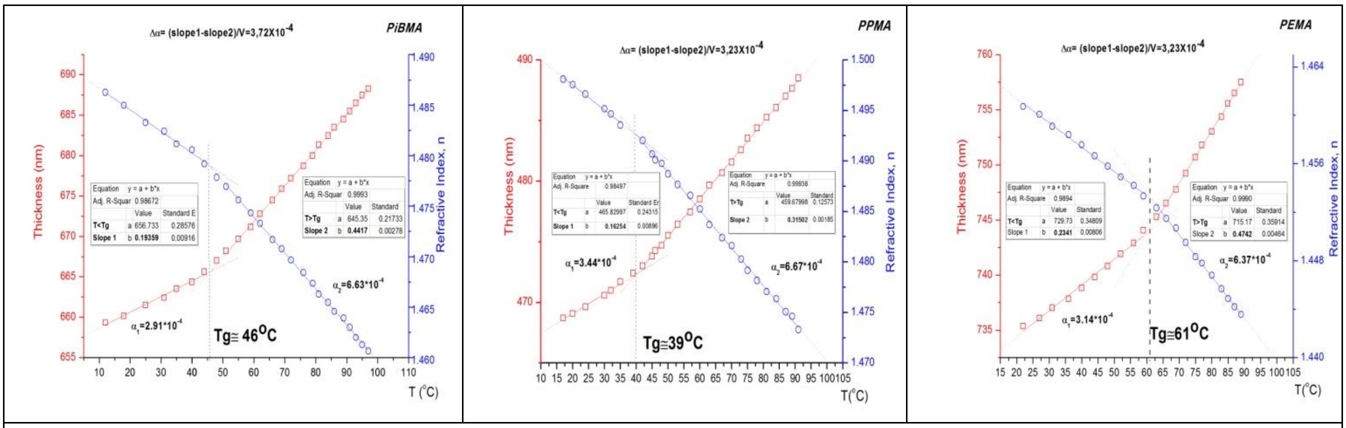


Figure 1: Thermal treatment of methacrylate films and monitoring of film thickness and refractive index a) PiBMA, b) PBMA, c) PEMA. The calculated values of thermal expansion coefficients, depending on the temperature range, are : (i) $2.9\text{-}3.4*10^{-4}$ for T<Tg a value of and (ii) $6.4\text{-}6.7*10^{-4}$ for T>Tg. These values are in agreement with the bibliography data for these poly(alkyl methacrylates) [4].

Conclusions: The glass transmission temperature of polymeric films was measured with an FR-Basic equipped with the FR-Thermal kit. In a similar way other thermal parameters of polymeric films can be also determined e.g. Degradation temperature of polymeric films.

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[2] Y. Diamant, S. Welner and D. Katz, J. Polymer, "Glass transition temperatures of crosslinked poly (isobutyl methacrylate)" 1970, 11, 498-506,

[3] S. S. Rogers and L. Mandelkern, J. Phys. Chem., "Glass formation in polymers. I. The glass transitions of poly(n-alkyl metacrylates)" 1957, 61, 985–991

[4] J. E. Mark, "Physical Properties of Polymers Handbook", Springer, 2007