Interfacial Effects in Montmorillonite Filled Polyester Thin Films

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Abstract: The behavior of thin supported and non-supported films has been shown to be distinct from the bulk polymer. Separately, high surface area fillers such as montomorillonite layered silicates (MLS) result in improved properties. In this study, we investigate thin films of polyethylene terephthalate (PET) with MLS. The thermal expansivity and glass transition temperature (T_g) were determined using ellipsometry. The results show that with increasing MLS concentration, the glass transition drops for the thin and thick film plateaus. For intermediate thicknesses, a modest influence of the MLS polymer interface on the characteristic length is found. The liquid layer thickness decreases with increased MLS presence.

Keywords: Thermal expansivity, Glass transition, Thin film, Montmorillonite layered silicates, Nanocomposite.

INTRODUCTION

Polymeric thin films and coatings are used for many applications from microelectronics to food packaging. The properties of polymer films in the range of nanometer or tens of nanometers often differ substantially from the bulk polymer. Therefore, the study of thin film properties is very significant. The differences between bulk and confined geometry dynamics have been associated with interference of intrinsic length scales with the dimensions of imposed geometry. These size effects can also be related to the surface and the interface effects. The free surface of a supported film is more mobile than the bulk polymer film [1]. The mobility of the interface is dependent on the interaction between the film and the substrate. Weak or unfavorable interactions between the film and the substrate result in increased mobility at the interface. Strong interactions with the substrate may lead to few layers of the molecules being strongly immobilized [2].

The glass transition temperature, T_g has been considered in much detail, especially in terms of how it affects either supported [3-6]. or free standing [6] films or glass forming liquids confined in nanoscopic pores [4]. This has been ascribed to specific chain organization such as conformation, orientation or chain packing due to a fluctuation in local density [2] and is supported by molecular simulations [5], as well as experimental results. The chain density and therefore the glass transition has been shown to increase, decrease or not change with decreasing thickness [6]. The differences have been attributed to confinement geometry, the particular polymer investigated, experimental method and measurement technique sensitivity. Ellison and Torkelson [7] established increased breath of relaxation in thin coated films. Their work utilizes fluorescent probe molecules [8]. Campbell *et al*., [9] studied T_g and CTE of poly (n-alkyl methacrylate)s films of thickness ranging from 7 to 200 nm. They observed T_g and CTE of thin films of poly (n-alkyl methacrylate)s deviates from bulk film for films thinner than

approximately 60 nm. From the experimental results they observed the significant reduction in deviation in T_g and CTE of thin film from bulk film as the alkyl chain length was increased from methyl to n-octyl. They attributed to increase in the cooperative segmental length with the addition of solvent. Utilizing a combination of polymer physics (molecular mobility) and polymer miscibility (interactions), Pham and Green [10] explain the contradictory T_g-thickness results *via* a three layer model. Next to a substrate, the polymer chains bend and fold over leading to higher density, decreased mobility and higher glass transition temperatures. At the free surface, lower density, higher mobility and lower glass transitions are to be expected. The higher mobility results from an increase in relaxation time due to entropic effects such as disentanglements, confinement effects or by chain-end segregation. Between the free surface and the region close to the substrate, polymer chains have intermediate mobility. When the substrate-polymer interaction is non interacting, the thickness of the substrate layer is lower than when there is a high degree of substrate-polymer interaction. The consequence is that the intermediate region in a non-interacting coating is thicker than in an interacting system. In the former the glass transition increases with increasing film thickness. The free surface mobility dominates leading to decreased T_g's with decreasing film thickness. In a film where positive substrate-polymer interactions occur, the glass transition decreases with increasing film thickness as the lower mobility layer dominates.

The coefficient of thermal expansion (CTE) has also been determined to have thickness dependence [2]. The dependence is more pronounced for ultra thin films and arises due to structural differences and density. Prior results show that as the samples become thicker, the thickness dependence is diminished and the effective CTE approaches bulk properties. An increasing CTE with decreasing thickness was attributed to the increased contribution of a liquid like layer with CTE of ultra thin films approaching melt values [11]. Polymer nanocomposites based on the dispersion of clays, such as montomorillonite layered silicate (MLS) have shown promise as organic-inorganic hybrids with the potential to improve mechanical [12], thermal [13] and barrier properties

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[14]. In this paper we report the effects of montomorillonite layered silicate dispersion on the CTE and T_g of polyethylene terephthalate (PET) polymer thin films of varying thicknesses. We utilize ellipsometry to determine thickness changes with temperature and consequent changes in the T_g and CTE.

EXPERIMENTAL

Sample Preparation

PET pellets (Kosa 1101) were dried overnight in a vacuum (-100KPa) oven at 65°C. A 10% by weight masterbatch of MLS (Cloisite 30B) was prepared on a Werner Pfleiderer co-rotating twin screw extruder with an L/D ratio of 30. Individual MLS concentrations of 1, 2, 3 and 5% by weight were processed on a Leistritz counter rotating twin screw extruder of 30 mm screw diameter and an L/D ratio of 32.5. A high shear screw with kneading block and reverse element was chosen to achieve uniform distribution of MLS (30B). The processed composites were dissolved in dichloroacetic acid and heated at 60 °C for 18 hours. Films were spun on silicon wafer substrate from the solution on a photoresist spinner; model PWM 32, Headway Research Inc. Texas, USA. The native oxide on the silicon wafers was etched using 2 wt % hydrofluoric acid. Immediately after removing the native oxide from the Si wafer, thin films were deposited on the Si wafer by the spin casting method, using varying speeds from 300-3000 rpm and viscosity to control the thickness. Films were annealed at 60°C for 3 hrs and 120 °C for 24 hours to remove the entrapped solvent. Annealing was done in steps to avoid any pore formation in the thin film. Thickness of the samples is determined on the samples within a week of sample preparation.

Experimental

A HSC302 hot stage from Instec, Inc. with temperature controller was connected to a Sentech SE 800 spectroscopic ellipsometer for heating the film and controlling the temperature. Heating was performed at a rate of 2 °C /min. Procedures outlined by Kawana and Jones [15] were employed to ensure accuracy of measurements. Ellipsometric angles, Ψ and Δ were measured over a temperature range of 30-140 °C. Using the Cauchy model [16], the thickness was determined from these parameters as a function of temperature and plotted. The coefficient of thermal expansion and glass transition temperature were calculated from the data. The thickness was determined over the temperature range of 30-140 °C in steps of 10 °C. Each sample was held at a constant temperature for 5 minutes before the measurement. The thickness of the sample was cross verified by thickness measurement using cross sectional scanning electron microscopy. The thickness is measured by ellipsometry are within 7% error. T_g were determined as the intersection of two slopes between change of length to original length over the temperature change. The CTE is calculated as ratio of change of length to original length per degree Centigrade. CTE and T_g values were determined for thicknesses from 25 nm to 720 nm.

RESULTS AND DISCUSSION

The dispersion of MLS in thin polymeric films was studied by optical microscopy and grazing angle X-ray diffraction (GAXRD). As seen in Fig. (**1**), polarized optical microscopy images show that the dispersion of the layered silicates in the film is uniform. The GAXRD results in Fig. (**2**) show a very small broad peak of MLS at 5.8º and 8.5º 2Θ value for the 5% MLS concentration film. These peaks confirm that the platelets are well dispersed (Note the absence of the primary 001 reflection at 2.9º). The thickness of the film was measured as a function of temperature. The thickness was verified from the cross sectional SEM and the thickness measured from the ellipsometry are within 7% error. The ratio of change of thickness to original thickness with temperature for pure PET and the nanocomposite thin films are shown in Fig. (**3**) for samples of 80 nm thickness. The glass transition temperature is reported as the intersection of the two slopes of thermal expansion over the temperature range of 30-140 °C. In Fig. (**4**), we show the measured values of the glass transition for the PET and three samples having varying MLS concentrations. Thick films approach a constant value. The transition from thin film to bulk plateau occurs in the same thickness range for both the PET and MLS containing films with the T_g of the PET being consistently higher. The decreasing trend in T_g with MLS concentration is the same for samples below 80 nm and above 220 nm while in the transition region, differences between the PET and the MLS containing films is negligible. We note that the spun cast PET films showed a significantly higher thick film plateau T_g value than bulk free standing films. We attribute the difference to the solution processing and changes in crystallinity between free standing films and solution cast films. Slow crystallization kinetics [17], coupled with inhibited crystallization in thin semi-crystalline films [18] can explain the differences. As Fig. (**1**) indicates, polarized optical micrographs indicated an absence of birefringence and no crystallites in the cast films. With a decreased crystallization in the thin films relative to the bulk, an increase in T_g is likely [17].
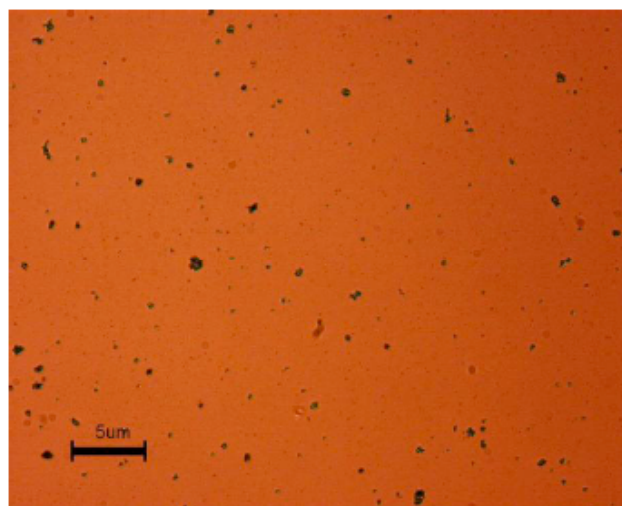

Fig. (1). Polarized optical micrograph of PET+ 5 % MLS nanocomposites showing dispersion of MLS.

The pre, post T_g and difference between post and pre Tg CTE for pure PET and for the nanocomposite thin films is shown in Fig. (**5a**, **b** and **c**) respectively. We observed a decrease in CTE with increasing MLS content for a given thickness. CTE decreased from 9.1 X10^{-4} to 7.6X10^{-4} / °C for the pure polymer to the nanocomposite with 5% MLS for a 25 nm thick film. In the post T_g region, thicknesses above 450 nm did not show a difference with or without the
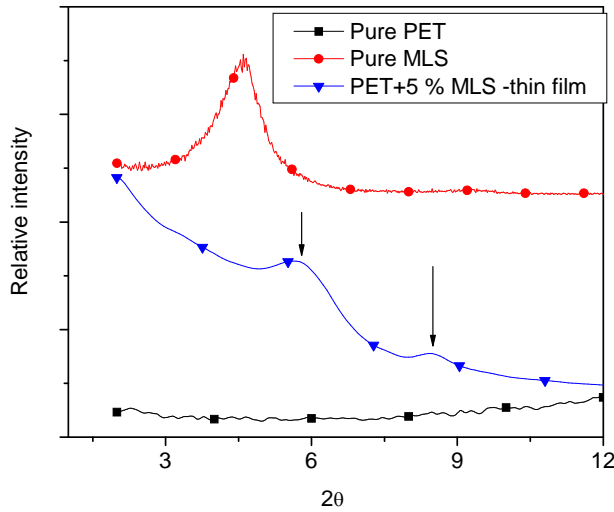
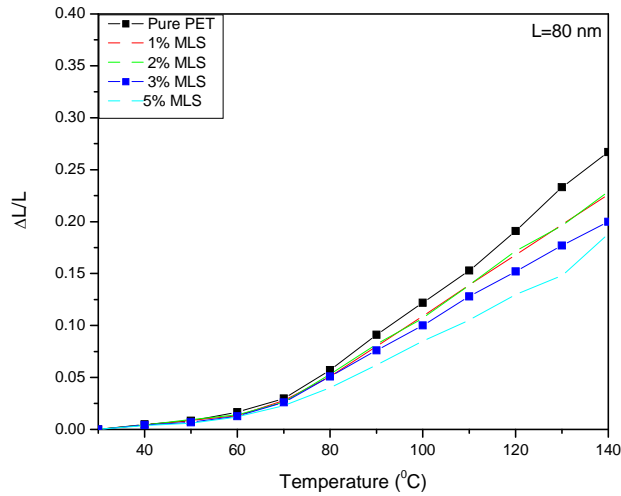**Fig. (2).** X-ray diffraction of PET nanocomposite thin film.

Fig. (3). Ratio of change of thickness to original thickness with temperature in pure polymer and nanocomposites.
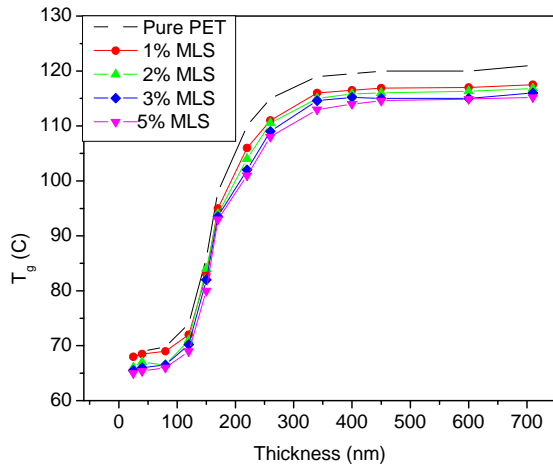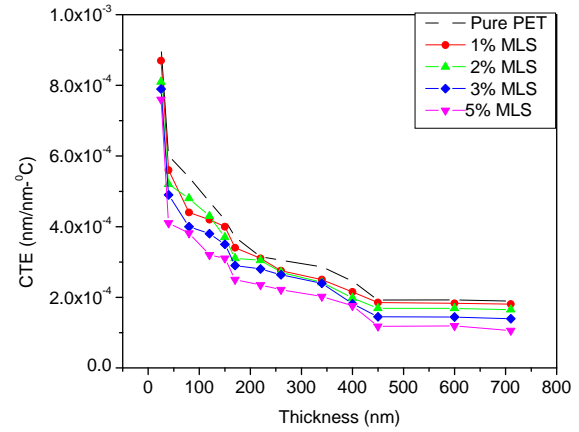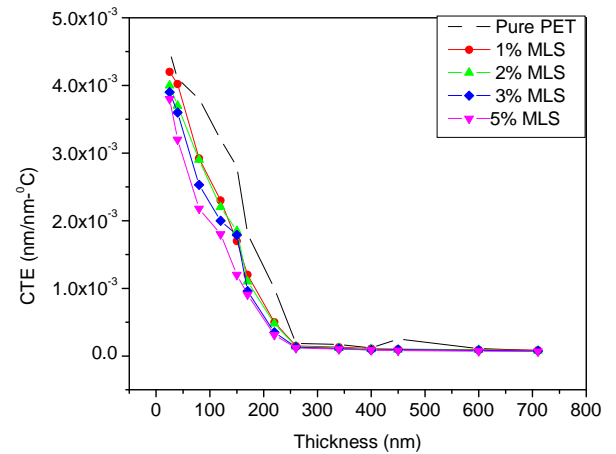

Fig. (4). Variation of glass transition temperature (T_g) with thickness for pure PET and PET+5% MLS thin film.

presence of MLS. This indicates the contributions of MLS-polymer interaction area are significant in the pre-T_g region.
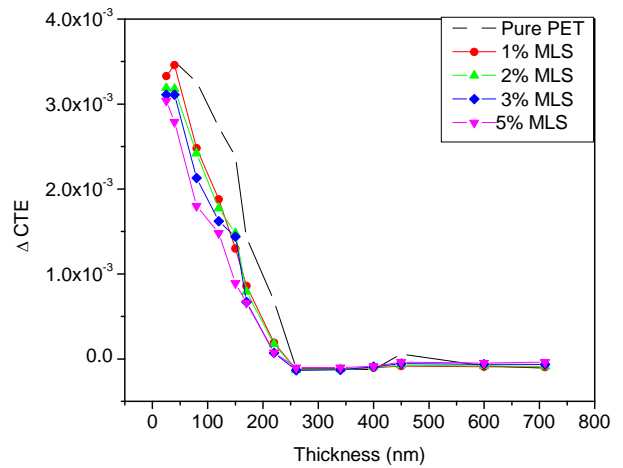
The post and pre-T_g differences show a drop with increased thickness similar to reported previously by Kim *et al.*, [19]. The CTE initially decreases drastically and then begins to plateau with increasing film thickness. If the mobility of the polymer near the substrate is significant, then the CTE decreases with increasing film thickness. On the other hand, if

a

b

c

Fig. (5). a. CTE as a function of thickness and MLS before T_g.

b. CTE as a function of thickness and MLS after T_g.

c. Difference of CTE as a function of thickness and MLS before and after T_g.
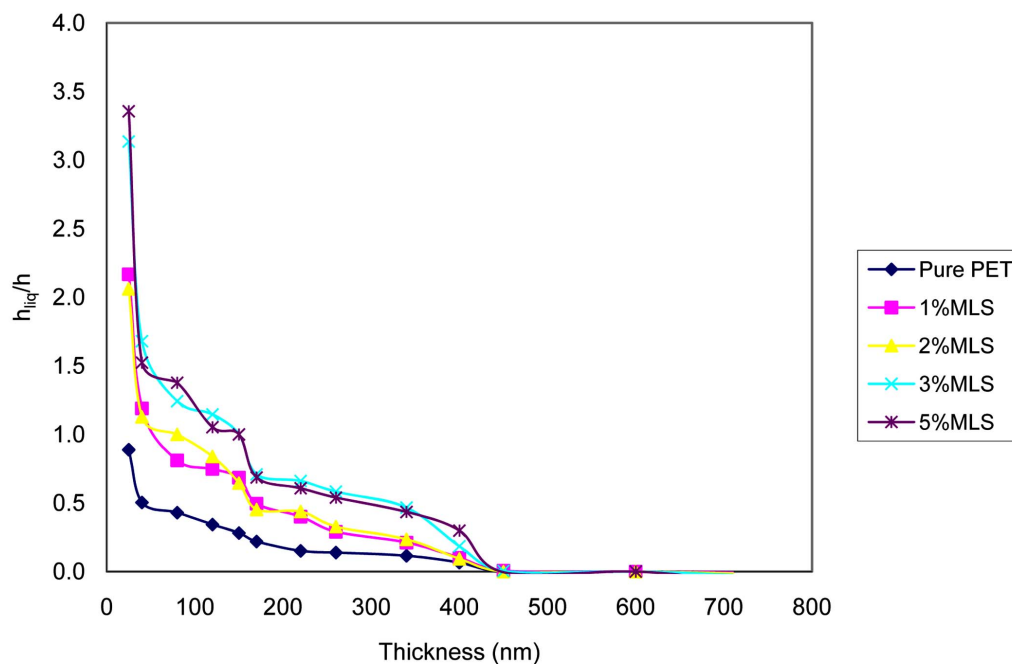
Fig. (6). Fraction of liquid layer for a given thickness.

the mobility of the polymer near the surface of the film is increased and the free surface mobility is dominant, CTE increases with increasing film thickness. The spin coating process leads to an orientation in the in-plane direction, which gives a strong covalent bond while the interchain forces out-of plane are dominated by weak Van der Walls force. Thus most volumetric expansion is directed in the thickness direction and this effect is more pronounced for thinner films. Thus initially thinner films have higher CTE. The CTE decreases for thicker films due to their higher density.

Along the lines of Keddie *et al.*, [14] and Kawana and Jones [18] we use a layer model with the value of the higher mobility surface layer weighted by the relative thickness of the surface layer. Thus

$$\alpha(T) = \frac{h_{liq}(T)}{d}\alpha_{liq}(T) + \left(1 - \frac{h_{liq}(T)}{h}\right)\alpha_{glass}(T)$$

Where h is the total film thickness, $h_{liq}(t)$ is the thickness of the surface liquid like layer and $\alpha_{liq}(T)$ and $\alpha_{glass}(T)$ are the expansivities of the liquid and glass states respectively. If we regard the behavior of the 400 nm film as essentially bulk like we can use the values of $\alpha_{liq}(T)$ and $\alpha_{glass}(T)$ deduced from these curves to invert equation 1 and use it with our experimentally determined expansivity-temperature data to deduce the thickness of the surface liquid like layer $h_{liq}(T)$. Inverting we get

$$\frac{h_{liq}}{h} = \frac{(\alpha(h) - \alpha_{glass})}{(\alpha_{liq} - \alpha_{glass})}$$

The results are shown in Fig. (**6**). As can be seen, similar to results reported by Keddie *et al.*, [14] the CTE increases with decreasing thickness indicating an approach to melt values. The increased surface area of the MLS nanocomposites results in increased liquid layer fractions with increasing concentration.

CONCLUSIONS

We studied the effect of film thickness on T_g and CTE for pure PET and nanocomposite films. We observed an increase of 40 ºC in T_g for 220 nm film thickness compared to bulk film. The transition thickness in the PET was higher than that recorded in pure amorphous polymers such as polystyrene. The addition of nanoclay to pure PET film decreased the T_g with increased MLS concentration. The drop in T_g with MLS concentration was dominant in the plateau regions of the thin and thick films. The film thickness dependence did not change and a similar transition thickness breadth occurred with or without MLS being present. The CTE of the film decreased when thickness increased from 25 nm to 710 nm for pure PET and 5% MLS concentration film by 79% and 86% respectively. Though we did not observe a large change in T_g with the addition of MLS, CTE decreased by 40% for films of 450 nm thickness. When the predicted CTE value is compared with the experimental value, it is clear that there is strong interaction between the MLS and the polymer in thin polymer films. From the T_g and CTE data, it is very clear that with the addition of MLS, the interaction between the nanoclay and polymer has increased. The presence of nanocomposite interfaces based on fillers with high surface area changes the thickness of the liquid layer.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Mansfield, K.F.; Theodorou, D.N. Molecular dynamics dimulation of a glassy polymer surface. *Macromolecules*, **1991**, *24*(23), 6283-6294.

[2]   van Zanten, J. H.; Wallace, W.E.; Wu, W. Effect of strongly favorable substrate interactions on the thermal properties of ultrathin polymer films. *Phys. Rev. E*, **1996**, *53*(3), R 2053-2056.

[3]   Forrest, J.A.; Dalnoki-Veress, K.; Dutcher, J.R. Interface and chain confinement effects on the glass transition temperature of thin polymer films. *Phys. Rev. E*, **1997**, *56*(5), 5705-5716.

[4]   Jackson, C.L.; McKenna, G.B. The glass transition of organic liquids confined to small pores. *J. Non-Cryst. Solids*., **1991**, *131-133*, 221-224.

[5]   Torres, A.; Nealy, P.F.; de Pablo, J.J. Molecular simulation of ultrathin polymeric films near the glass transition. *Phys. Rev. Lett.*, **2000**, *85*(15), 3221-3224.

[6]   Alcoutlabi, M.; McKenna, G.B. Effects of confinement on material behavior at the nanometer size scale. *J. Phys: Cond. Mat.*, **2005**, *17*, R461-R524.

[7]   Ellison, C.J.; Torkelson, J.M.; Distribution of glass-transition in nanoscopically confined glass formers. *Nat Mater*., **2003**, *2*, 695-700.

[8]   Ellison, C.J. ; Torkelson, J.M. Sensing the glass transition in thin and ultrathin polymer films *via* fluorescence probes and labels. *J. Polym. Sci. Pol. Phys.,* **2002**, *40*(24), 2745-2758.

[9]   Campbell, C.G.; Vogt, B.D. Examination of the influence of cooperative segmental dynamics on the glass transition and coefficient of thermal expansion in thin films probed using poly(n-alkyl methacrylate)s. *Polymer*, **2007**, *48*(24), 7169-7175.

[10]   Pham, J.Q.; Green, P.F. The glass transition of thin film polymer/polymer blends: Interfacial interactions and confinement. *J. Chem. Phys*., **2002**, *116*(13), 5801-5806.

[11]   Keddie, J.L.; Jones, R.A.L.; Cory, R.A. Size-dependent depression of the glass transition in polymer films. *Europhys. Lett*., **1994**, *27*(1), 59-64.

[12]   Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. Synthesis of nylon 6-clay hybrid by montmorillonite intercalated with daprolactam. J. *Polym. Sci. A: Polym. Chem.*, **1993**, *31*(4), 983-986.

[13]   Zeng, C.; Lee, J.L. Poly(methyl methacrylate) and polystyrene/clay nanocomposites prepared by in-situ polymerization. *Macromolecules*, **2001**, *34*(12), 4098-4103.

[14]   Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. Synthesis and Properties of Polyimide-Clay Hybrid. *J Polym. Sci. Part A: Polym. Chem,.* **1993**, *31*(10), 2493-2498.

[15]   Kawana , S.; Jones, R.A.L. Character of the glass transition in thin supported polymer films. *Phys. Rev. E*, **2001**, *63*, 021501/1-6.

[16]   Sentech SE 800 Spectroscopic Ellipsomter, Reference manual, **2006**.

[17]   Massa, M.V.; Carvalho, J.L.; Dalnoki-Veress, K. Confinement effects in polymer crystal nucleation from the bulk to few-chain systems. *Phys. Rev. Lett.*, **2006**, *97*(24), 247802/1-4.

[18]   Beers, K.L.; Douglas, J.F.; Amis, E.J.; Karim, A. Combinatorial Measurements of Crystallization Growth Rate and Morphology in Thin Films of Isotactic Polystyrene. *Langmuir*, **2003**, *19*(9), 3935-3940.

[19]   Kim, J.H.; Jang, J.; Zin, W. Thickness dependence of the glass transition temperature in thin polymer films. *Langmuir*, **2001**, *17*(9), 2703.