Polymer 42 (2001) 6419–6423

polymer

www.elsevier.nl/locate/polymer

Glass transition of ultra-thin films of modified PVC

Y. Grohens[a,*], J. Sacristan[b], L. Hamon[a], H. Reinecke[b], C. Mijangos[b], J.M. Guenet[a]

[a]Institut de Chimie des Surfaces et Interfaces, CNRS, 15, Rue Jean Starcky, BP 2488, 68057 Mulhouse Cedex, France
[b]Instituto de Ciencia y Tecnologia de Polimeros, CSIC Juan de la Cierva 3, 28006 Madrid, Spain

Received 22 January 2001; received in revised form 16 February 2001; accepted 26 February 2001

Abstract

Ultra-thin layers ($h = 50–150$ nm) of PVC, functionalised in solution by thiophenol (t-PVC) and 4-aminothiophenol (am-PVC), were prepared by spin-coating on silicon wafers. The glass transition temperature of these thin films was investigated by kinetic scan ellipsometry. The Tg of the am-PVC and t-PVC modified PVC is found to increase more strongly with the degree of modification in thin layer geometry than in the bulk. Also, Tg(h) of t-PVC exhibits a larger increase in the confined state as compared to am-PVC. This result is unexpected since no specific interactions are assumed between thiophenyl group and the surface indicating that other driving forces for the alteration of Tg(h) should be taken into account.

In a second step, the supported PVC thin films are chemically cross-linked in solution by terephthaloyl chloride. The Tg(h) of the polymer layer increases with the cross-linking time more severely at a higher degree of modification but independently of the thickness of the layer indicating that the diffusion process is not altered in thin layers. Above Tg, the thermal expansion coefficient α of the thin films is not modified after cross-linking, whereas, it was found to decrease strongly between 4 and 8% of modification in the uncured state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Glass transition; PVC; Terephthaloyl chloride

1. Introduction

Much attention has been paid in recent years to the particular properties of polymer chains confined in thin film geometry [1–11]. These thin films are of growing interest in industrial applications such as electronic packaging, protective coating and adhesion. The geometric and enthalpic constrains generated by the presence of a solid surface have been shown to modify deeply the conformation [1], the dynamics [2] or the dewetting behaviour [3] of the polymer.

The glass transition temperature of thin layers of polymers has been investigated by many groups in the past few years [4–11]. One of the main conclusion that can be drawn from these works is that the Tg of thin films decreases for weakly interacting systems [4–7] and increases on strongly attractive surfaces [5–9]. In the case of freely standing PS films, Tg decreases much more rapidly with decreasing film thickness than for supported films [4]. Polymers at free surfaces or in contact with repulsive surfaces are claimed to be dominated by entropic effects such as disentanglements, confinement effects or by chain-end segregation which leads to a Tg depression [8]. In contrast, the increase of Tg for PMMA or poly-2-vinylpyridine (P2VP) thin layers, as occurs on strongly attractive substrates, is often ascribed to specific chain organisation (conformation, orientation) or chain packing (local density fluctuation) [7,11]. The diffusion in thin films can also be modified with respect to the bulk as reported by several workers [12–15]. Indeed, the decrease of the diffusion coefficient was claimed for the interdiffusion of polymers chains in thin films involving a motion of the whole chain [12–13] while enhancement in translational diffusion of chromophores was also reported in the same geometry [14]. Moreover, it was stated by other workers [15] that the diffusion of residual solvent in ultra-thin films can be substantially hindered.

PVC can be chemically functionalised in solution and in the melt using thiol compounds [16]. The degree of modification can be tuned between 0 and 30% by controlling the time, the temperature and the proportion of solvent/non-solvent used in the reaction. Moreover, the modified PVC can be chemically cross-linked by terephthaloyl chloride in solution. In this paper, we report on an investigation of the glass transition of pure and modified PVC in thin layer geometry. The influence of the degree and the nature of the modification on Tg were examined. The supported PVC films at various degrees of modification were

---

[*] Corresponding author.
E-mail address: y.grohens@univ-mulhouse.fr (Y. Grohens).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00171-9

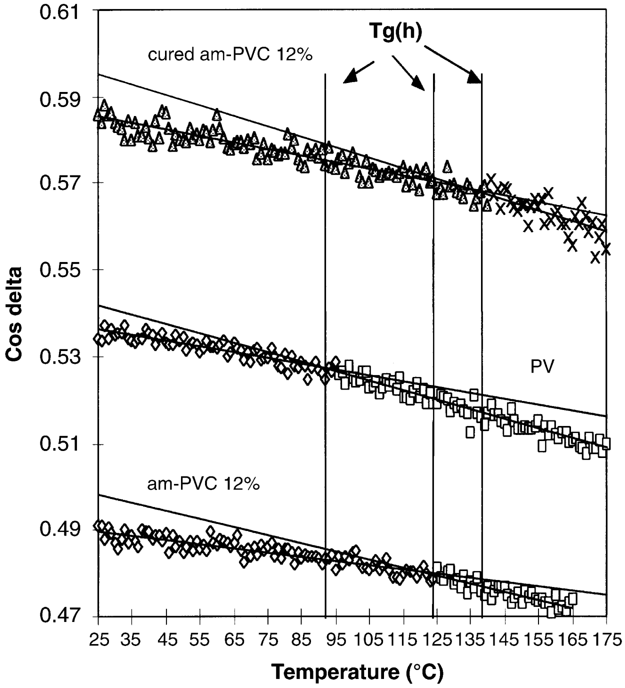

Fig. 1. Evolution of the cos delta ellipsometric angle as a function of temperature for 50 s cured am-PVC 12% (upper curve), non-modified PVC (middle curve) and 12% am-PVC (lower curve) 50 nm thin films on silicon wafer.

chemically cross-linked for different times and the Tg and thermal expansion of the resulting samples were studied.

2. Experimental

Commercial bulk polymerised atactic PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were $M_W = 112{,}000\ \mathrm{g\ mol^{-1}}$ and $M_N = 48{,}000\ \mathrm{g\ mol^{-1}}$. PVC powder modification was done with aminothiophenol (am-PVC) or thiophenol (t-PVC) according to reference [16].

These polymers were spin cast from cyclohexanone solutions on (111) silicon wafers. The substrates were treated during at least 2 h in an UV–ozone chamber prior to polymer deposition. The polar character of the surface was highlighted by contact angle measurements which provide values of the dispersive and polar surface energy of $\gamma_s^d = 39$ mN m^{-1} and $\gamma_s^p = 36$ mN m^{-1}, respectively. The thickness variation (50–150 nm) was achieved by varying the concentration of the solution (20 and 40 g L^{-1}). The spin coated samples were studied after annealing at Tg + 70°C, for at least 24 h and cooled at constant rate. Cross-linking of the samples was done by dipping the film and the substrate in a 0.1 M solution of terephthaloyl chloride in toluene, at 0°C. In order to study the kinetic of cross-linking in thin films, the samples were removed from the solution at different reaction times, washed with toluene and dried in an oven above Tg for 24 h under reduced pressure in order to remove any trace of residual solvent.

The Tg of the bulk polymer samples, was investigated by DSC at a heating rate of 2°C min^{-1}. Spectroscopic ellipsometry experiments were performed by using a Sopra ES4M apparatus, equipped with a heating rate programmable hot-stage, working in a range of wavelength from 0.4 to 0.8 μm. For the measurements of both film thickness and expansion coefficients, the ellipsometric angles were recorded at stabilised temperatures increased by 10°C increments. The fit of the ellipsometric angles tan ϕ and cos Δ in the overall range of frequency allows the calculation of thickness and refractive index of the layers. The so-called kinetic ellipsometric scans are performed at a heating rate of 2°C min^{-1}. The experimental data points are divided in two sets of points corresponding to temperature range below and above the estimated rupture in the slope. The points are fitted using a linear least-square routine. The range of temperature is changed by step of 2°C to find the best fit for the two lines. The experimental glass transition temperature of a thin film of thickness h, Tg(h), is defined as the temperature where the two lines intersect.

3. Results and discussion

From DSC investigations of bulk samples, Tg is found to be 105 ± 3°C for am-PVC and 75 ± 2°C for t-PVC, both modified at 20%, whereas the bulk Tg of non-modified PVC lies at 87 ± 1°C. A depression in Tg occurs when introducing a thiophenyl group in the PVC chain whereas the presence of an amine group located on the thiophenol modifier increases the Tg of the bulk PVC. The increase of the bulk glass transition, Tg^b, of am-PVC with the side-chain modification is ascribed to an increase in the strength of the inter-molecular interactions, through H-bonding between the polar side-groups. Actually, the existence of these specific interactions can cause a decrease in the degree of freedom of the side-chain along with a decrease in the free-volume. Conversely, repulsive interactions between thiophenyl groups in t-PVC lead to a decrease of the bulk Tg.

Fig. 1 shows that the Tg of PVC ultra-thin films can be determined from the kinetic ellipsometric scans performed at one wavelength, namely, 0.75 μm. The break in the slope of the curves cos $\Delta = f(T)$, due to an increase in the thermal expansion of the PVC layer, corresponds to the change from the glassy to the rubbery state, i.e. to the glass transition. The Tg measured for the non-modified PVC 50 nm film is Tg(h) = 95 ± 3°C, whereas, it was only Tg^b = 87°C for the same PVC in the bulk. This 8°C increase of Tg is probably due to favourable interactions taking place between the PVC chloride atoms and the silicon substrate. The evolution of the Tg(h) of the modified PVC is much more striking. The modification of the PVC increases the Tg(h) of a 50 nm thin film to 155 and 120 ± 3°C for thiophenol and aminothiophenol, respectively. The increase of Tg(h) in the thin layer

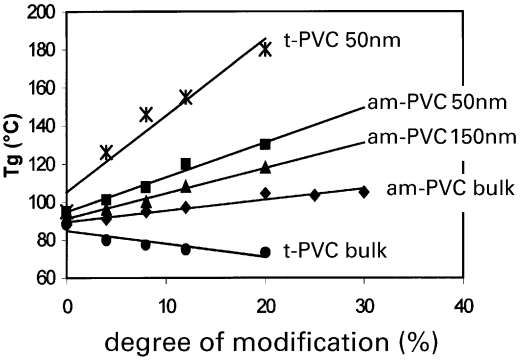

Fig. 2. Evolution of the Tg as a function of the degree of modification for (●) bulk t-PVC, (◆) bulk am-PVC, (▲) 150 nm thin film of am-PVC, (■) 50 nm thin film of am-PVC and () 50 nm thin film of t-PVC.

of am-PVC is due to the attractive interactions involving the amine function of the polymer side-groups and the silanols of the Si–O_x covered silicon surface. The presence of specific interactions, such as H-bonds [17], has been shown to strongly influence the Tg(*h*) of PMMA on silicon [9], for instance. Kinetic ellipsometric scan experiments performed on a 50 nm thin film of am-PVC 12% spin coated on silicon wafers covered by a thin gold evaporated layer were carried out. No modification in Tg(*h*) was observed in that particular case where no specific interactions can be developed between the polymer and the substrate. This is a strong evidence of the significant influence of specific interactions on the Tg(*h*).

Nevertheless, restriction of the discussion to the effect of the nature of the interfacial interactions is limiting. Indeed, the sulphur group, located at the junction of the chain backbone and the bulky side-group in t-PVC, is not at a favourable position for interacting specifically with the surface because of steric constrains. Other type of interactions, such as attractive van der Waals forces or Coulombic interactions can be envisaged. Moreover, the effect on Tg can also be due to modifications of entropic factors of the chains induced by the presence of thiophenol side-groups in the PVC which could, in turn, influence the chain packing near the interface. Functionalising the PVC by aminothiophenol group instead of thiophenol, is likely to modify the stiffness of the chains. This last parameter has already been pointed out as a significant factor on the adsorption process [18] and in the Tg(*h*) of thin layer [19].

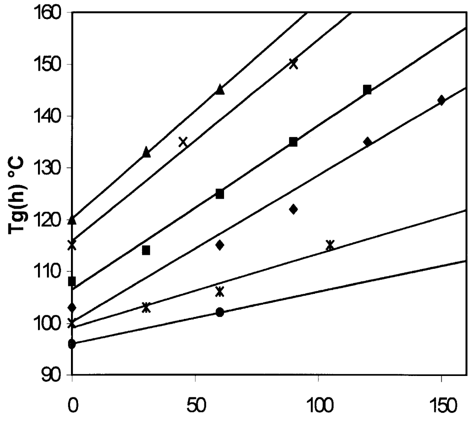

Fig. 3. Evolution of the Tg with the cross-linking time for thin layers of am-PVC. (●) represents a 150 nm film modified at 4%, (ж) a 50 nm film modified at 4%, (◆) a 150 nm film modified at 8%, (■) a 50 nm film modified at 8%, (×) a 150 nm film modified at 12% and (▲) a 50 nm film modified at 12%.

Fig. 2 shows the linear increase of Tg with the increase of the degree of modification of the am-PVC and t-PVC in thin films. Confining am-PVC in the thin layer, i.e. $h = 150$ or 50 nm, which corresponds, approximately, to 12 and 4 times the radius of gyration of the PVC chains, respectively, increases Tg(*h*) more severely than in the bulk. At the solid interacting surface, aminothiophenol side-groups are likely to be stuck to the surface and the density of segments pinned to the surface increases with the degree of modification. The higher the density of segments bonded to the substrate, the longer the time for large scale relaxation of constrains generated during the spin-coating process for the am-PVC. It is worth noting, from the slight increase of Tg(*h*) for pure PVC thin films, namely 8°C, that the energy of interaction of the chloride group with the substrate is likely to be weaker than the interaction energy of the modified side groups with the surface. However, the behaviour of the 50 nm thin film of t-PVC is more striking. As discussed previously, no strong specific interactions with the surface are expected with that polymer. Therefore, from the observation made on this system, purely enthalpic considerations should not only be taken into account to explain the evolution of Tg(*h*). Entropic constrains generated in the thin layer should also be considered. Thus, the spin-coating process is assumed to induce a deformation of the chains that cannot relax even after very long annealing times [11]. The chains in thin film of modified t-PVC are, therefore, suggested to be frozen-in in non-equilibrated conformational states. The possible adsorption of aggregates or surface aggregation of modified polymer chains formed in solution could be responsible, to some extent, of changes in the packing density at the film/silicon interface [20] which are likely to strongly modify the Tg(*h*).

In order to improve the thermal stability of the thin films, often required for industrial applications in electronic devices for instance, we have used the amine functionality of the am-PVC to chemically cross-link the polymer in situ in the thin layer. The chemical curing reaction offers the advantages of preventing thermal or photo-degradation in the film often encounter in other cross-linking methods. However, since the reacting species have to diffuse through the layer, the increase of the Tg(*h*) recorded for the thin polymer layers could modify the translational motion of the reactants and hinder the reaction of aminothiophenol side-groups buried in the film. Indeed, several workers have reported that the diffusion of chromophores [14,15]

Table 1
Coefficient of thermal expansion and Tg of bulk and thin film PVC obtained from ellipsometric experiments for the thin films. PVC * refers to coefficient of thermal expansion drawn from literature [21] for the bulk PVC

Thermal expansion coefficient	Tg (°C)	Below Tg (K^{-1})	Above Tg (K^{-1})
Bulk PVC *	87 ± 1	6.9×10^{-5}	1.7×10^{-4}
Pure PVC (150 nm)	90 ± 3	1.9×10^{-4}	5.6×10^{-4}
am-PVC 4% (150 nm)	93 ± 3	1.8×10^{-4}	5.2×10^{-4}
am-PVC 8% (150 nm)	98 ± 3	1.5×10^{-4}	1.9×10^{-4}
am-PVC 12% (150 nm)	105 ± 4	1.3×10^{-4}	1.8×10^{-4}
Cured am-PVC 12% (150 nm)	137 ± 4	1.1×10^{-4}	1.8×10^{-4}

can be enhanced by the presence of a solid surface at a distance evaluated at about 4 radius of gyration, Rg. Furthermore, The diffusion coefficient of the bulk PVC is $D=1\times10^{-6}\ m^2\ s^{-1}$ for ethanol vapour at 30°C [21]. Roughly 50–100 s would be required for this small molecule to diffuse through a 150 nm film. Although our experiments are carried out at 0°C and the therephtaloyl chloride molecules are bigger than ethanol, diffusion of reactive molecules through the overall thickness of the films can occur in the time scale of our experiments.

Fig. 3 shows that Tg(h) increases linearly with the curing time independent of the film thickness and the degree of PVC modification. Moreover, it can be noticed that the slope of the curves increases with the degree of modification independent of the film thickness. Finally, Tg(h) remains lower, at a given reaction time, for the 150 nm films than for the 50 nm films. These observations allow us to conclude that the curing reaction proceeds without any perturbation due to the presence of a solid underlying attractive surface. The efficiency of the cross-linking agent is not strongly altered. Indeed, the large increase of Tg(h) at high degrees of PVC modification indicates that the cross-linking density of the network increases in the thin layer. Therefore, a sufficient amount of cross-linking agent is capable to reach the reactive sites of the polymer even below the Tg of the bulk polymer and well below the Tg of the polymer in the thin layer.

The thermal expansion coefficient normal to the surface $\alpha_N = 1/h(dh/dT)$ of the thin films can be calculated from the spectroscopic ellipsometry experiments carried out at different temperatures. The thermal expansion of the 150 nm layers below Tg(h) is roughly identical, namely 1.8×10^{-4}–$1.1\times10^{-4}\ K^{-1}$ for pure PVC, modified PVC or cross-linked PVC. In contrast, above Tg(h) the expansion coefficient α_N for pure PVC and am-PVC 4% is 5.6×10^{-4} and $5.2\times10^{-4}\ K^{-1}$, respectively, which is significantly higher than for the am-PVC at 8 and 12%, i.e. $1.8\times10^{-4}\ K^{-1}$ but also higher than the bulk thermal expansion as shown in Table 1. This result accounts for a stronger decrease of the packing density of the chains with temperature for pure and 4% modified PVC in the thin layer, as compared to those of 8 and 12% am-PVC but also as compared to the bulk. A transition in the expansion coefficient occurs for a small amount of modified side-groups, i.e. between 4 and 8%. No further decrease in α_N is observed by increasing the degree of modification. Surprisingly, as indicated in Table 1, the chemically cross-linked samples do not exhibit any further decrease in the thermal expansion of the layer as would be expected in the bulk. The chemical bridging between the chains induces no decrease in the variation of the packing density within the cured thin layers with the temperature. Furthermore, the refractive index of the thin films remains unchanged after curing indicating that no increase in the density of the layer occurs in the cross-linked samples. These results yield the conclusion that the packing density in a thin layer is mainly governed by the conformation adopted by the chains at an interface and that chemical cross-linking does not strongly modify this arrangement. Moreover, in the course of curing, the non-equilibrium conformation in the thin layer, as suggested above, could be preserved and, therefore, participate to the strong increase of the Tg(h). Finally, AFM investigation of the thin films reveals that the roughness of the samples remains unchanged before and after curing with a calculated R_a value equal to 0.3 nm in average.

The unexpected effects of the chain modification of PVC on the Tg(h) in thin films were highlighted in this work. The origin of the driving force for the modification of the Tg of confined polymers is still an open question. The nature of the interfacial interactions is not the only significant parameter and entropic factors of the chains should be taken into account. In addition, besides fundamental outcomes, this system is a promising route to achieve resistant, thermally stable surface protective ultra-thin films.

References

[1] Frantz P, Granick S. Macromolecules 1995;28:6915.
[2] Arndt M, Stannarius R, Groothues H, Kremer F. Phys Rev Lett 1997;79:2077.
[3] Reiter G. Macromolecules 1994;27:3046.
[4] Forrest JA, Dalnoki-Veress K, Stevens JR, Dutcher JR. Phys Rev Lett 1996;77:2002.
[5] Keddie JL, Jones RAL, Cory RA. Faraday Discuss 1994;98:219.
[6] Keddie JL, Jones RAL, Cory RA. Europhys Lett 1994;27:59.
[7] Van Zanten JH, Wallace WE, Wu W. Phys Rev 1996;E53:R2053.
[8] Prucker O, Christian S, Bock H, Ruhe J, Frank CW, Knoll W. Macromol Chem Phys 1998;199:1435.
[9] Grohens Y, Brogly M, Labbe C, Schultz J. Langmuir 1998;14:2929.

[10] Jones RAL. Curr Opinion Colloids Interface Sci 1999;4:153.
[11] Overney RM, Buenviaje J, Luginbuhl R, Dinelli RJ. Therm Anal Calorimetry 2000;59:205.
[12] Lin EK, Wu WL, Satija SK. Macromolecules 1997;30:7224.
[13] Frank B, Gast AP, Russel TP, Brown HR, Hawker C. Macromolecules 1996;29:6531.
[14] Hall DB, Miller RD, Torkelson JM. J Polym Sci: Part B: Polym Phys 1997;35:2795.
[15] Frank CW, Rao V, Despotopolou MM, Pease RFW, Hinsberg WD, Miller DD, Rabolt JF. Science 1996;273:912.
[16] Sacristan J, Reinecke H, Mijangos C. Polymer 2000;41(15):5577.
[17] Fowkes FM. J Adhesion Sci Tech 1987;1:7.
[18] Bernstein TM, Zhulina EB, Skvortsov AM. Biopolymer 1979;18:1171.
[19] Kim JH, Jang J, Zin WC. Langmuir 2000;16:4064.
[20] Lipatov YS. Polymer reinforcement. Canada: ChemTech Publishing, 1995.
[21] Brandrup J, Immergut EH, editors. Handbook of polymers 3rd ed. New York: Wiley, 1989.