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Comparison of differential scanning calorimetry, FTIR, and NMR to measurements of adsorbed polymers☆

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ABSTRACT

Temperature modulated differential scanning calorimetry (TMDSC) measurements on samples with very small amounts of polymers adsorbed on silica particles have been contrasted with spectroscopic techniques (FTIR and NMR) on the same or similar systems. The results are consistent in that the hydrogen bonding of the polymers to surface silanols reduces the mobility of some of the adsorbed polymer segments and results in higher glass transition temperatures for those polymer segments. These experiments reinforce the notion of an interface that is graded in terms of mobility. In contrast to bulk polymers, where the glass transition process can be considered spatially homogeneous, interfacial polymers can be considered heterogeneous on the scale of the interface. The results also suggest that the heterogeneous nature of the interfacial polymers and various sensitivities of the different techniques may result in apparently different conclusions about the surface effect and its reach.

1. Introduction

Polymers adsorbed at interfaces are difficult to characterize, but they are of importance in many applications, from structural composites to electronics. The physical properties of composites, for example, may be significantly influenced by thin layers of polymers at the interface between the dissimilar materials. One difficulty in the characterization of the properties of these layers is their thinness, i.e., there is little material in what can be considered to be the interfacial region. In many cases, techniques useful for more bulk-like materials, e.g. polymers, either do not work or need modification for application to interfacial materials.

In many systems, polymer composites are used or created in such a way that interfacial polymers are not simply found on the “outer surface” of the structures. Instead, there may be multitudes of “inner” surfaces or interfaces, such as in particle- or fiber-filled composites. Consequently, many useful techniques that rely on scattering, reflection, or absorption from the outer surfaces are not particularly useful for the inner surfaces. Fortunately, there are some techniques that can be used to probe the inner surfaces. In our group, we have focused on NMR and temperature modulated differential scanning calorimetry (TMDSC) that naturally probe the whole material. To a lesser extent, infrared spectroscopy has also been used, as samples filled with particles that are small enough, can be relatively transparent to infrared radiation.

There are few works that provide a good overview of some of the polymer-surface attributes [1–4] with a special emphasis on the glass transition of adsorbed polymers. It is clear from these reports that the nature of adsorbed polymers is complicated and, in some cases, apparently conflicting results have been reported. One might expect apparently conflicting results when different techniques, with varying sensitivities, are applied to these complex systems.

A number of specialized thermal techniques and novel instrumentation has been developed for the characterization of small amounts of adsorbed polymers or ultrathin polymer layers. Some of the specialized techniques were designed to tackle the sensitivity problems. Local thermal analysis [5,6], ultrafast heating of thin films [7–9], thermally stimulated current DSC [10,11], differential chip calorimeters [12], and temperature modulated DSC (TMDSC) [13–17] have been used. These experiments demonstrate the need for high sensitivity and also highlight the effects of the strength of interaction of the polymer with the surface on the T_g as the results often depend on the systems studied.

The purpose of this present paper is to review some studies of the thermal analysis of adsorbed polymers and relate these studies to other (mainly spectroscopic) studies of adsorbed polymers on the same or similar systems. In particular, the work involves the characterization of polymers on oxide particles, primarily silica. It is our purpose to demonstrate that the information from the various techniques was consistent with respect to the behavior of adsorbed polymers. However, different studies may lead to

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dissimilar conclusions if the techniques used are sensitive to different portions of the absorbed polymers.

2. Experimental

Samples were usually produced by the adsorption of polymers from solution. A general procedure for typical samples is given here. Massed amounts of polymer were dissolved in solvents, often toluene, and then the solutions (ca. 10 mL) were added to measured amounts of solid substrates (ca. 0.3 g) in test tubes. Sometimes the substrates were wetted with solvent before the addition of the polymer solutions. The samples were then mixed in a mechanical shaker for 48 h, centrifuged at 2500 rpm for 1 h, and then the supernatant liquids were decanted. The decanted solutions were sometimes used to provide an additional measurement of the adsorbed amount of polymer. The samples were then dried with either a flow of air or nitrogen. The adsorbed samples were then dried in a vacuum oven for about 24 h. In some cases, the polymer dispersions were rinsed, centrifuged, and decanted a few more times to remove loosely- or non-adsorbed polymers. In other cases, after decantation, the remaining polymers in solution were allowed to adsorb during the drying process. Either way, after temperature cycling of the final product, the polymer behavior was primarily affected by only the adsorbed amount of polymer and not by the exact nature of how it got there.

For silica substrates, Cab-O-Sil silica (Cabot Corp., Tuscola, IL, USA) was used. This material has a high surface area (for example, M-5P has 200 m^2 surface/g silica) and is non-porous (i.e., it is not silica-gel like with pores). The silica was usually dried at 450 °C in an oven before use. Different polymers from different sources were used, some purchased and some made in our laboratory. The molecular masses are identified in the text, where appropriate. The polymers used were generally characterized using gel permeation chromatography (GPC) with a light scattering and refractive index detector (Dawn EOS and Optilab, Wyatt Technology, Santa Barbara, CA, USA).

The amounts of polymer adsorbed were estimated from thermogravimetric analysis (TGA) with a TGA 2950 (TA Instruments, New Castle, DE, USA) thermogravimetric analyzer. The samples were heated from room temperature to 700 °C at 20 °C/min in air. Sometimes a small mass loss of between 100 and 300 °C was believed to have been due to entrapped small molecules (solvent). The mass loss of the organic material (around 350–400 °C) and that of the remaining substrate were used to estimate the fraction of polymer originally present.

Differential scanning calorimetry measurements were made using a DSC 2920 (TA Instruments, New Castle, DE, USA) [18]. A variety of sample conditions were used and some typical ones are as follows. The samples were referenced with an empty pan with a 50 mL/min nitrogen stream. The samples were heated to well above their bulk T_g for at least 5 min, cooled to well below the T_g and held for several minutes, and then heated (usually at 2.5 °C/min) with a modulation rate of 1.00 °C/min. The second heating scans were reported so that the recent thermal histories for the samples were the same. Either the reversing heat flow rate, or the derivative of the reversing heat flow rate, was plotted. For adsorbed samples, a 10 °C running average was often used to reduce the higher frequency noise. The reported T_gs were taken as the maximum of the derivative of the heat capacity curves.

The NMR spectra were taken with on a Varian VXR-400/S NMR spectrometer operating at 61.395 MHz for deuterium. No significant changes in the spectra were noted due to temperature cycling. A fixed frequency wide-line probe was used (Doty Scientific, Columbia, SC, USA) with an 8 mm diameter coil. A 2.7 μs pulse, fast digitizer, and quadrupole echo sequence were used for the spectra in wide-line mode.

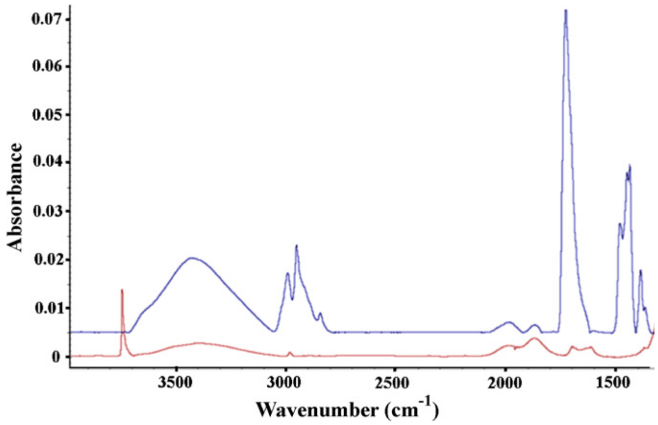

Fig. 1. FTIR spectrum of Cab-O-Sil (lower) and 0.6 mg/m^2 PMMA adsorbed on Cab-O-Sil (upper). The resonance at 3745 cm^{-1} is from the free surface silanols on Cab-O-Sil.

3. Results and discussion

3.1. Bulk and adsorbed polymers – heterogeneity in the glass transition region

The FTIR spectra for Cab-O-Sil silica and PMMA (450 kg/mol) adsorbed on Cab-O-Sil are shown in Fig. 1. Since the particle size of Cab-O-Sil was quite small (primary particles on the order of 100 nm), the FTIR spectrum can be obtained in transmission mode [19,20]. The spectrum of the silica shows a sharp resonance at around 3745 cm^{-1} due to the presence of isolated surface silanols [21]. There were also some weaker resonances due to the silica. The region below around 1400 cm^{-1} is not shown, as it had very intense absorptions from the silica, which are not of interest to this work. Fig. 1 also shows that the intensity of the resonance from the surface silanols was considerably reduced when PMMA was adsorbed on the silica. This reduction in intensity was consistent with H-bonding of the surface silanols, including H-bonded silanols that exhibit a broad band around 3645 cm^{-1}. The spectrum with PMMA also includes resonances for aliphatic stretches (C–H around 3000 cm^{-1}) and carbonyl stretches (C=O around 1730 cm^{-1}).

For PMMA adsorbed on silica, an attractive interaction between the polymer and silica was expected. PMMA and related polymers have hydrogen bond acceptors (the carbonyl groups) and the silica has hydrogen bond donors (surface silanols). The reduction, and in some cases, the elimination of the isolated surface silanols, was an indication that H-bonding occurred. Additional evidence for H-bonding can be found based in the carbonyl-stretching region [19,20,22]. Shown in Fig. 2 is the expansion of the FTIR spectrum in the region of the carbonyl stretch. In contrast to the carbonyl resonance in the spectrum of the bulk polymer, that for the adsorbed polymer was asymmetric. The figure shows an example of spectral simulations with contributions from free (bulk-like, centered at 1734 cm^{-1}) and hydrogen-bonded (bound, centered at 1708 cm^{-1}) carbonyls. Based on these simulations, it was possible to estimate the fraction of bound carbonyls in the adsorbed polymer. Unfortunately, the molar absorptivities of the bound and free carbonyls were different, so a direct comparison of the integrated intensities was not appropriate. Consequently, a method was developed to extract the ratio of the absorptivities of the free and bound carbonyls from the fitting of the spectra at different adsorbed amounts [20]. The method was based on the assumption that a thin layer of adsorbed polymer (effectively carbonyl groups) was attached to the surface of the silica. This layer, considered to be "tightly-bound", does not actually represent a true, distinct polymer layer, but is symbolic of the amount of material adsorbed

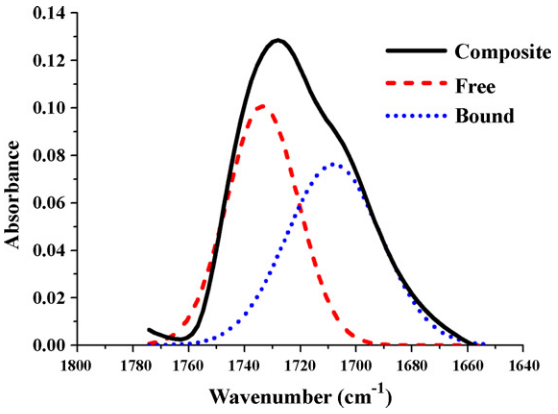

Fig. 2. FTIR spectrum of the carbonyl stretching region for PMMA adsorbed on Cab-O-Sil showing the component spectra due to free (1734 cm^{-1}) and hydrogen-bonded (1708 cm^{-1}) carbonyls.

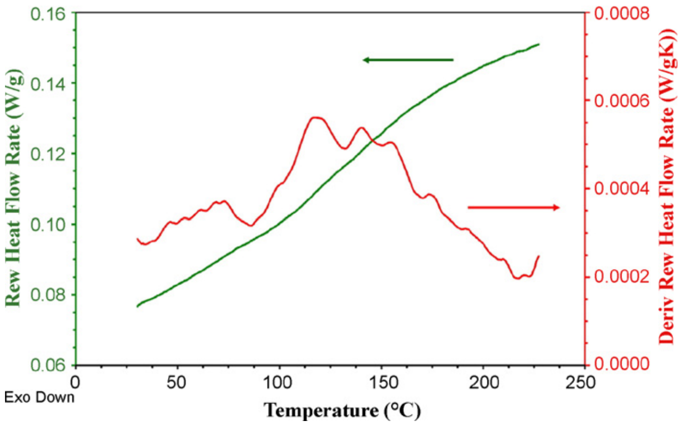

Fig. 4. DSC thermogram for adsorbed PMMA on silica (0.80 mg/m^2) showing the heat flow rate and also the derivative of the heat flow rate.

in an “equivalent” layer. Polymers (carbonyls), added in excess of this amount, were considered to be “loosely-bound”, almost bulk-like.

A plot of the fraction of tightly-bound carbonyls, *p*, from the FTIR experiment, as a function of the adsorbed amount is shown in Fig. 3. Also shown in this figure are similar results from the TMDSC experiments (vide infra). The FTIR results are well represented by a smooth curve based upon the assumption of a layer of tightly-bound polymer in the equivalent of 0.17 mg/m^2. The method also showed that the adsorbed carbonyls have a much greater apparent absorptivity (by almost a factor of 8 for PMMA) than the free carbonyls do [20]. This difference highlights the effect of the H-bonding in the spectrum and makes it easier to quantify the amount of bound carbonyls. The different symbols in Fig. 3 represent polymers of varying molecular mass (32, 85, and 450 kg/mol) and those deposited from different solvents (filled for toluene or unfilled for benzene/acetonitrile). To a first approximation, the most important variable is the adsorbed amount. Compared to that of the adsorbed amount, *p*, from TMDSC (vide infra), the bound fraction for FTIR is much smaller.

The TMDSC thermogram of PMMA (90 kg/mol) adsorbed on silica is shown in Fig. 4 for a sample with 0.80 mg/m^2. It is clear from the reversing heat flow curve that there was thermal activity extending well beyond the range of the glass transition of the bulk polymer. We have preferred to plot the derivative of the reversing heat flow rate for adsorbed polymer transitions because it allows the broad transitions to be more easily seen. When the T_g is estimated from the maximum in the heat flow derivative curve, it is a few degrees higher than that from the heat flow curves. It should also be noted that because of the breath of the transition, filling factors (i.e., the presence of the silica), thermal contact and conductivity of the coated particles, and, perhaps, different changes in heat capacity for the adsorbed polymer (ΔC_p, compared to bulk), the thermal behavior of the polymer is more difficult to characterize (lower sensitivity) than that of bulk polymers.

It is well known that the T_g of PMMA depends on the tacticity of the polymer [23]. For the 90 kg/mol PMMA (Fig. 4), it was reported that the bulk T_g was about 108 °C with a transition width of about 11 °C [13]. When this material was adsorbed at about 0.8 mg/m^2 on silica, a very broad transition was found that was centered at around 130 °C with a transition width of about 60 °C [13]. Thus, the transition was moved to a higher temperature and broadened with adsorption. Undoubtedly, this effect was due to the H-bonding of the carbonyls and silica, reducing the mobility of the polymer segments. Unlike the FTIR case, the distance scale over which the TMDSC measured properties of the adsorbed polymer were altered by the interaction with the silica was not as clear.

The thermograms for adsorbed PMMA on silica vary as a function of the adsorbed amount and examples of these are shown in Fig. 5. At the lowest amount of polymer (ca. 10% PMMA or 0.65 mg/m^2), it is difficult to discern any thermal transition from the polymer. At ca. 30% PMMA (2.33 mg/m^2), a broad transition with high temperature activity in the thermogram (from about 120–170 °C) was observed.

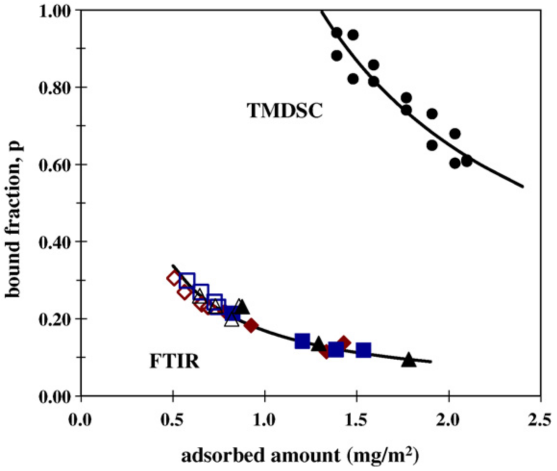

Fig. 3. Bound fractions of PMMA, *p*, from FTIR (carbonyls, lower) and TMDSC (upper).

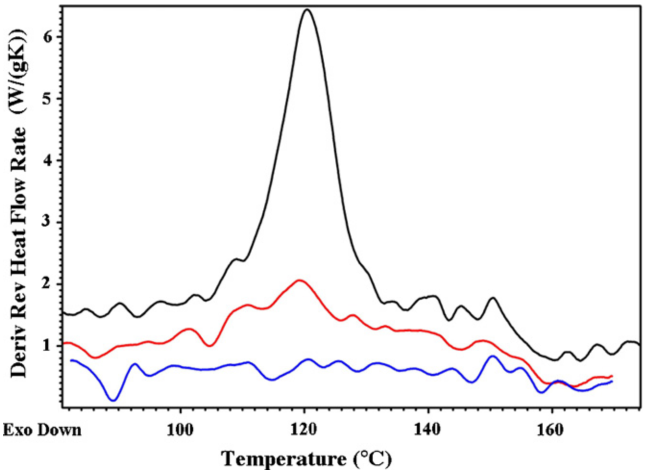

Fig. 5. The derivative of the heat flow rate for PMMA adsorbed on silica as a function of temperature for 10% (bottom), 30% (middle) and 70% (top) PMMA.

The material responsible for most of this broad transition was considered tightly-bound. A small peak around 120 °C was also present. At larger amounts of polymer (70% PMMA or 12.1 mg/m^2), a larger peak grew in around 120 °C attributed to the loosely-bound polymer. For this, and other samples at larger adsorbed amounts, the thermograms were superpositions of tightly- and loosely-bound contributions. These thermograms were consistent with a model in which there was a fixed amount of tightly-bound PMMA beyond which additional polymer was loosely-bound [15]. Based on this model, the two-component behavior of a series of thermograms for PMMA (with different adsorbed amounts) was analyzed [15]. A complicating factor was that the ΔC_p values for the tightly- and loosely-bound polymer segments were not necessarily the same (similar to the case for the absorptivities in FTIR). In order to take this effect into account, a model similar to the one used for FTIR was proposed. This model, when applied to the TMDSC data for the adsorbed PMMA samples, yielded the results for the adsorbed amount, p, shown in Fig. 3. The amount of polymer that was tightly-bound was considerably larger than that estimated by the FTIR experiment. While the FTIR experiments were only sensitive to segments directly bound to the surface via the carbonyls, the TMDSC experiments showed, that many more segments, well beyond those directly attached, were affected by adsorption.

From the TMDSC experiments, the equivalent thickness of the tightly-bound layer was determined to be 1.3 mg/m^2 [15]. The analysis also was used to estimate the ΔC_p in the glass transition region, yielding ΔC_p(tightly-bound)/ΔC_p(loosely-bound) = 1/6. This reduction in ΔC_p has the unfortunate consequence of making the tightly-bound segments even harder to observe in the TMDSC experiment. An alternative possibility is that over the temperature range measured, some of the polymer remained glassy, or had a glass transition that was so broad that it was not observed. This missing polymer would result in an apparent ratio of the ΔC_ps of less than 1. At the present time, neither alternative has been definitively proven. However, since the change of the heat capacity of the polymer is related to the modes of motion through which energy can be placed, one might expect that polymer segments close to bound sites (e.g., those bound carbonyls observed in the FTIR experiments) should have a lower ΔC_p than the bulk polymer. In any case, the TMDSC experiments were sensitive to many segments altered by the presence of the surface and that, compared to bulk, the glass transition (mobility) of the adsorbed polymer was heterogeneous.

The results of other kinds of estimates of bound segments from other experiments have been compared. However, unlike the present study, most have focused on polymer dispersions (solvent present), not the dry state. Barnett et al. [24] have used solid and liquid echoes to distinguish between mobile (loosely-bound) and rigid (tightly-bound) segments in adsorbed polymers. Robb and Smith [25] have compared results from NMR, ESR, and IR of adsorbed polymers and the differences gave information about the confirmation of the polymer at the interface. The combination of NMR and DSC has also been useful to determine the nature of phase transitions and interfaces [26]. Finally, when a variety of polymers in dispersions are compared [1], the picture is consistent. FTIR measurements are very short range and magnetic resonance and calorimetry measurements are more sensitive to longer-distance scales associated with their longer-range phenomena.

To reinforce the concept of the heterogeneity of dynamics of adsorbed polymers, a comparison of the deuterium NMR spectrum for a high molecular mass poly(vinyl acetate)-d$_3$ (PVAc-d$_3$) in bulk and adsorbed on silica is shown in Fig. 6. Comparable experiments with PMMA have not been done because they are in a much higher temperature range than for PVAc, which is in a convenient temperature range. For the ^{2}H NMR experiments, the T_g for bulk PVAc-d$_3$ was found to be about 36 °C higher than that found for the bulk polymer [27,28]. This difference is consistent with that expected from time–temperature superposition principles [28]. Well below the T_g(NMR) for bulk PVAc, a Pake pattern was found for the glassy polymer, and at high temperatures, a much narrower single resonance was found for the rubbery polymer. In between, an intermediate pattern is found in the glass transition region.

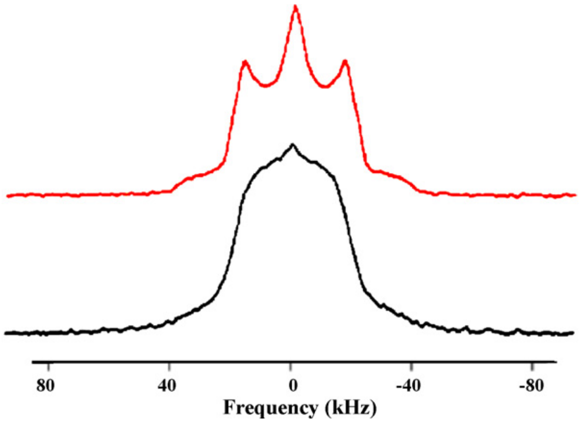

Fig. 6. Solid-state ^{2}H NMR spectra of PVAc-d$_3$ in bulk (lower) and at 0.36 mg/m^2 adsorbed on silica (upper) at 68.8 °C. The spectrum of the adsorbed polymer shows the presence of segments that were more mobile and those that are less mobile than those in the bulk polymer.

A spectrum for a sample of bulk PVAc-d$_3$ in this region (68.8 °C) is shown in Fig. 6. For contrast, a spectrum for adsorbed PVAc-d$_3$ (0.72 mg/m^2) is also shown in the figure. For the adsorbed polymer (Fig. 6), a spectrum that was heterogeneous was observed. A Pake powder pattern was superimposed on a narrow central resonance at this temperature. In fact, the adsorbed polymer had some segments that were more mobile, and some that were less mobile than bulk. The more mobile segments were assigned to those at the polymer–air interface and the less mobile segments were assigned to those at the polymer–silica interface. The integrated intensity of the more mobile segments, in this case, is quite small, underscoring the sensitivity of the NMR method, as compared to TMDSC [29]. Evidence for these assignments includes experiments for poly(methyl acrylate)-d$_3$, where the enhanced mobility of the polymer at the polymer–air interface was reduced when a polymer overlayer was placed on top of the interfacial layer [30]. These studies confirm the notion of heterogeneity of the interfacial layers and also the concept of an interface graded in terms of mobility.

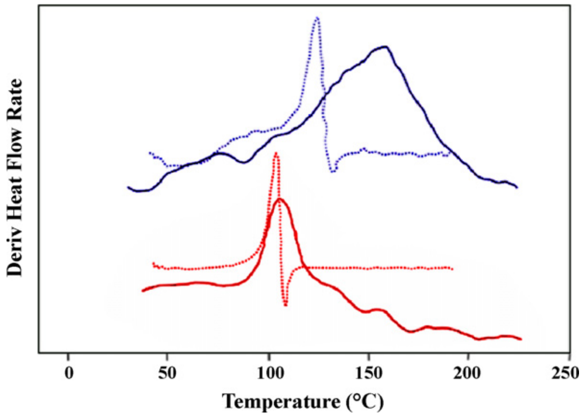

Fig. 7. Thermograms of PS (lower) and PMMA (upper) in bulk (dashed) and on silica (solid). The adsorbed amounts were 1.23 and 1.30 mg/m^2 for PS and PMMA, respectively.

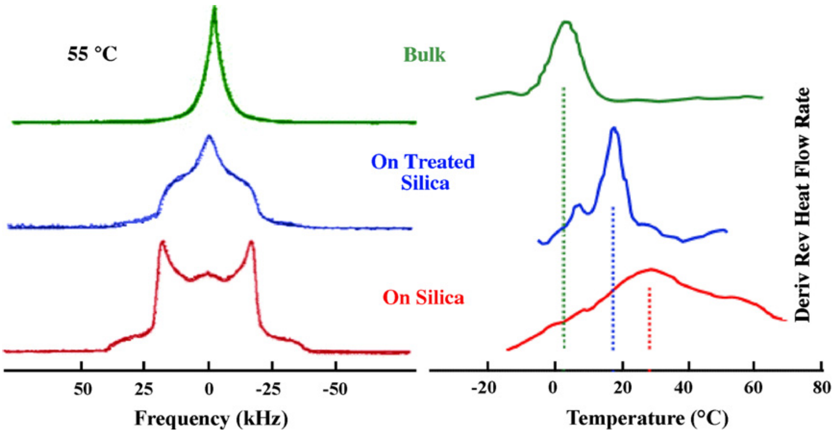

Fig. 8. Solid-state ^{2}H NMR spectrum of PMA-d_3 at 55 °C (left) and derivative TMDSC thermograms of PMA (right) in bulk (upper), on treated silica (middle), and on native silica (lower).

3.2. *Effect of surface treatment*

Comparisons of the thermograms for bulk and adsorbed PMMA and PS are shown in Fig. 7. For PS (52.4 kg/mol), the glass transition temperature (T_g) for the bulk polymer was about 104 °C and the transition was fairly narrow (about 6 °C) [14,31]. The transition for the adsorbed sample, with an adsorbed amount of 1.23 mg/m^2, was broader than that of the bulk sample (width 21 °C); however, the transition was centered at the same place as on the bulk polymer.

The thermograms for bulk and adsorbed PMMA are also shown in Fig. 7. The T_g for bulk PMMA was 125 °C for the 136 kg/mol polymer [31] which was primarily syndiotactic and, consequently, had a relatively high T_g [23]. Again the bulk polymer T_g was fairly narrow (12 °C), while that for the adsorbed polymer was much broader (almost 60 °C for a 1.30 mg/m^2) with the T_g as high as 159 °C [13,15].

PS does not strongly bind to the silica, as the interactions between the aromatic rings of the PS and the surface silanols are weak. The changes in T_g upon absorption were smaller for PS than those in systems with stronger interactions, like PMMA (or PMA or PVAc, for example) where the interactions were much stronger due to the hydrogen bonding between the surface silanols and polymer carbonyls. Thus, the dependence of the T_g of thin films, for example, should show the influence of the polymer-surface interactions [3].

Another way to modify the interaction of the polymer with the surface is by changing the nature of the surface. One way to accomplish such a change is to modify the surface of the silica using hexamethyldisilazane [32]. This reaction puts trimethylsilyl groups on the surface and the surface is referred to as methylated. A direct comparison of the ^{2}H NMR and TMDSC can be made for PMA-d_3 under different conditions, and examples of these are shown in Fig. 8. In bulk, the 55 °C NMR spectrum shows a narrow resonance for PMA-d_3, indicative of a rubbery polymer. The TMDSC thermogram shows a T_g around 3 °C, which is relatively narrow. In contrast, the polymer adsorbed on silica (0.84 mg/m^2) shows an NMR spectrum, indicative of glassy PMA-d_3; however, a small resonance in the middle of the powder pattern is probably due to the presence of end groups that are rubbery and have additional mobility at this temperature. A more detailed report of the effects of molecular mass has been published [33]. The molecular mass effects for adsorbed PMA were, surprisingly, non-monotonic.

On silica, similar to the behavior of PMMA, PMA-d_3 yielded a thermogram with a very broad glass transition region shifted to higher temperatures (Fig. 8). The variable temperature NMR spectra for PMA-d_3 on silica [33–35] were very consistent with the TMDSC data. The glass transition of the adsorbed PMA-d_3 was increased, and the rubbery segments became more apparent as the temperature increased.

The behavior of PMA-d_3 on treated silica (Fig. 8) was in between that of the bulk polymer and that of the polymer on silica. The NMR spectrum at 55 °C showed some residual powder pattern plus some rubbery material as a broad center resonance. The TMDSC thermogram for this sample was fairly narrow, but slightly increased in temperature. It is believed that the presence of unreacted surface silanols provided a location for some residual H-bonding to the polymer [16]. These bonded carbonyls probably provide a moderate increase in the T_g for the treated silica, as observed in the figure.

4. Conclusions

The major conclusion to be reinforced is that, in general, bulk polymers have dynamics that can be considered spatially homogeneous, whereas polymers adsorbed in small amounts on oxide surfaces can be considered spatially heterogeneous. In our studies we have primarily focused on polymers with strong physical interactions (H-bonds) with silica surfaces. Consequently, the glass transition for many of the polymer segments was shifted to a higher temperature. However, in some cases, a small amount of the polymer may have segments that are more mobile than those in the bulk polymer. Based on these observations, it is reasonable to conclude, that at least in the systems reported here, the adsorbed polymers can be considered either raised or lowered in T_g, compared to bulk. Depending on the technique and its sensitivity to these different segments, one might conclude, that either event happened. In fact, for high molecular mass PVAc, segments in the adsorbed polymer could be characterized by both a higher or lower T_g and these different segments may even be in the same molecule.

From the standpoint of thermal analysis, the glass transition region for the adsorbed polymers is much broader than that for bulk polymers. The sensitivity of the transitions for adsorbed polymers, as dictated by the ΔC_p, appears to be significantly smaller than that for bulk polymers, making the thermal characterization of the adsorbed materials more difficult. A two-state model based on tightly- and loosely-bound segments for the interfacial polymer can be used to fit both thermal analysis and FTIR data for adsorbed polymers. The fraction of tightly-bound polymer from the TMDSC experiments is significantly larger than that from FTIR.

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References

[1] G.J. Fleer, M.A. Cohen-Stuart, J.M.H.M. Scheutjens, T. Cosgrove, B. Vincent, Polymers at Interfaces, Chapman & Hall, London, 1993.
[2] R.P. Wool, Polymer Interfaces: Structure and Strength, Hanser/Gardner Publications, Munich, 1995.
[3] J.A. Forrest, K. Dalnoki-Veress, Adv. Colloid Interface Sci. 94 (2001) 167–196.
[4] M. Alcoutlabi, G.B. McKenna, J. Phys.: Condens. Matter 17 (2005) R461–R524.
[5] D.S. Fryer, P.F. Nealey, J.J. de Pablo, Macromolecules 33 (2000) 6439–6447.
[6] D.S. Fryer, R.D. Peters, E.J. Kim, J.E. Tomaszewski, J.J. de Pablo, P.F. Nealey, C.C. White, W.L. Wu, Macromolecules 34 (2001) 5627–5634.
[7] M.Y. Efremov, E.A. Olson, M. Zhang, L.H. Allen, Thermochim. Acta 403 (2003) 37–41.
[8] M.Y. Efremov, E.A. Olson, M. Zhang, Z.S. Zhang, L.H. Allen, Macromolecules 37 (2004) 4607–4616.
[9] M.Y. Efremov, E.A. Olson, M. Zhang, S.L. Lai, F. Schiettekatte, Z.S. Zhang, L.H. Allen, Thermochim. Acta 412 (2004) 13–23.
[10] I.M. Kalogeras, Polymer 44 (2003) 4817–4827.
[11] I.M. Kalogeras, E.R. Neagu, Eur. Phys. J., E 14 (2004) 193–204.
[12] D. Zhou, H. Huth, Y. Gao, G. Xue, C. Schick, Macromolecules 41 (2008) 7662–7666.
[13] C.E. Porter, F.D. Blum, Macromolecules 33 (2000) 7016–7020.
[14] C.E. Porter, F.D. Blum, Macromolecules 35 (2002) 7448–7452.
[15] F.D. Blum, E.N. Young, G. Smith, O.C. Sitton, Langmuir 22 (2006) 4741–4744.
[16] M.T. Kabomo, F.D. Blum, S. Kulkeratiyut, S. Kulkeratiyut, P. Krisanangkura, J. Polym. Sci. B: Polym. Phys. 46 (2008) 649–658.
[17] A. Sargsyan, A. Tonoyan, S. Davtyan, C. Schick, Eur. Polym. J. 43 (2007) 3113–3127.
[18] S.L. Simon, Thermochim. Acta 374 (2001) 55–71.
[19] B.J. Fontana, J.R. Thomas, J. Phys. Chem. 65 (1961) 480–487.
[20] S. Kulkeratiyut, S. Kulkeratiyut, F.D. Blum, J. Polym. Sci. B: Polym. Phys. 44 (2006) 2071–2078.
[21] B.A. Morrow, A.J. McFarlan, J. Phys. Chem. 96 (1992) 1395–1400.
[22] H. Sakai, Y. Imamura, Bull. Chem. Soc. Jpn. 53 (1980) 1749–1750.
[23] J.M. O'Reilly, H.E. Bair, F.E. Karasz, Macromolecules 15 (1982) 1083–1088.
[24] K.G. Barnett, T. Cosgrove, B. Vincent, M. Cohen-Stuart, D.S. Sissons, Macromolecules 14 (1981) 1018–1020.
[25] I.D. Robb, R. Smith, Polymer 18 (1977) 500–504.
[26] M. Schonhoff, A. Larsson, P.B. Welzel, D. Kuckling, J. Phys. Chem. B 106 (2002) 7800–7808.
[27] F.D. Blum, G. Xu, M. Liang, C.G. Wade, Macromolecules 29 (1996) 8740–8745.
[28] R.R. Nambiar, F.D. Blum, Macromolecules 41 (2008) 9837–9845.
[29] F.D. Blum, W.Y. Lin, C.E. Porter, Coll. Polym. Sci. 281 (2003) 197–202.
[30] W.Y. Lin, F.D. Blum, J. Am. Chem. Soc. 123 (2001) 2032–2037.
[31] B. Zhang, F.D. Blum, Macromolecules 36 (2003) 8522–8527.
[32] S.V. Slavov, A.R. Sanger, K.T. Chuang, J. Phys. Chem. B 104 (2000) 983–989.
[33] B. Metin, F.D. Blum, J. Chem. Phys. 125 (2006), 054707/1–054707/9.
[34] W.-Y. Lin, F.D. Blum, Macromolecules 30 (1997) 5331–5338.
[35] W.Y. Lin, F.D. Blum, Macromolecules 31 (1998) 4135.