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Boonta Hetayothin

Frank D. Blum

Missouri University of Science and Technology

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THERMAL ANALYSIS OF ADSORBED POLY (VINYL ACETATE) ON SILICA

Boonta Hetayothin and Frank D. Blum

Departments of Chemistry, Materials Science and Engineering, and Materials Research Center
Missouri University of Science and Technology, Rolla, MO 65409-0010

Introduction

The physical properties of polymers at interfaces can be quite different from those in bulk due to the interaction between the adsorbed polymer and the surface. This phenomenon can be probed through the dynamic behavior of the polymer chains at the interface which can be experimentally probed by techniques such as nuclear magnetic resonance spectroscopy (NMR),¹ viscoelasticity, and calorimetry. At the polymer-air interface, polymer chains have more flexibility than those at the polymer-substrate interface. On the other hand, at the silica-polymer interface, where chains are more restricted on the surface, a higher glass transition temperature (T_g) results as compared with that for the bulk polymer. Adsorbed polymers like poly(methyl acrylate) (PMA) with different adsorbed amounts behave differently at the silica-polymer-air interface.² It was found that at low adsorbed amounts, the adsorbed polymer deviates significantly from the behavior of the bulk polymer. This behavior can be observed through measurement of the T_g .

In this paper, we report preliminary studies of the interfacial interaction of silica-polymer-air system through the glass transition from the thermal analysis point of view. Modulated differential scanning calorimetry (MDSC) is a widely used technique for identifying the T_g of polymers. Recently, we have reported the thermal behavior of poly(methyl methacrylate) (PMMA) and PMA adsorbed on Cab-O-Sil silica.^{3,4} In this work, we extend the observation to poly(vinyl acetate) (PVAc), an important polymer used in paints and adhesives applications where surface interactions are crucial to the performance of PVAc-containing system

Experimental

Medium molecular mass PVAc was used as received (Scientific Polymer Products, Inc., Ontario, NY). Cab-O-Sil MP-5 fumed silica (Cabot Corp., Tuscola, IL), with a surface area of 200 m²/g, was used as the substrate. The adsorbed PVAc on silica was prepared by dissolving a known amount of polymer in toluene and mixing the solution in centrifuge tubes with 0.2 g of silica.⁵ Mixing was done using a mechanical shaker for 48 h. Toluene was removed by passing air through the adsorbed polymer-silica mixture, while it was agitated. Then the adsorbed samples were dried in a vacuum oven at 40 °C for 24 h.

Thermogravimetric analysis (TGA) measurements were made using a Hi-Res TGA-2910 (TA Instruments, New Castle, DE) which was used to determine the amount of adsorbed polymer at the surface of the silica. TGA scans were run with a heating rate of 10 °C/min in air. The thermal behavior in the glass transition region was measured with a TA Instruments model 2920 MDSC (TA Instruments, New Castle, DE). One cooling scan and two heating scans were taken in the temperature range from -40 to 150 °C, at a rate of 10 °C/min, modulation amplitude of +/- 0.5 °C, and a period of 60 s. The second heating scan was used to determine the T_g from the reversing heat flow thermogram. The results are shown as differential reversing heat flow (dQ_{rev}/dT) vs temperature (T). A 10 °C smoothing was applied to the thermograms for the adsorbed samples.

Model

Recently, our research group described the thermal behavior of adsorbed polymer via a model with the assumption that there are two distinct types of adsorbed polymer segments. (A-loosely bound and B-tightly bound).³ A normalized polymer mass, m'_p , was defined as the total mass of adsorbed polymer (from TGA) divided by the mass of silica used, which is also the sum of the masses for the two components or

$$m'_p = m'_{pA} + m'_{pB} \quad (1)$$

The ratio of the heat flow changes of components A and B, given by r , is related to the ratios of the heat capacities of the components or

$$r = \Delta Q_A / \Delta Q_B = m'_{pA} \Delta C_{pA} / (m'_{pB} \Delta C_{pB}) \quad (2)$$

In effect, the ratio, r , is the ratio of the intensities in the thermograms. From eq. (2) and (3) a linear equation can be made or,

$$r = (m'_p - m'_{pB}) \Delta C_{pA} / (m'_{pB} \Delta C_{pB}) = [\Delta C_{pA} / (m'_{pB} \Delta C_{pB})] m'_p - \Delta C_{pA} / \Delta C_{pB} \quad (3)$$

This equation suggests that r should be linear function m'_p .

A previous study from our group has described the polymer behavior at the interface in terms of a bound fraction, f_B , which is the ratio of the mass of bound polymer at the interface to the total amount of polymer. It can be expressed as a function of the experimental observable, r , as

$$f_B = m'_{pB} / m'_p = m_{pB} / m_p = 1 / (1 + r \Delta C_{pB} / \Delta C_{pA}) \quad (4)$$

The fraction of bound polymer, f_B , can be estimated from the model by using the value of m'_{pB} obtained from the linear regression.

Results and Discussion

The thermograms of PVAc on silica for different adsorbed amounts are shown in Figure 1. The vertical scale in the thermograms has been shifted for comparison. The T_g of bulk PVAc was found to be 32 °C (at 10 °C/min) with a relatively narrow width compared to those in the adsorbed samples. The thermograms for the adsorbed PVAc on silica show two distinct peaks that we assign as component A (polymer-air interface, which is loosely bound where the T_g is close to bulk) and component B (silica-polymer interface which is tightly bound where the T_g is higher than that in bulk).

It is apparent that, as the adsorbed amount increases, the relative area under transition A increases, while that of transition B decreases slightly as shown in Table 1. While the amount of data collected to date is limited, the plot of the ratio, r , the ratio of the areas of the A and B components in the thermograms is linear function of the total relative mass of polymer (m'_p) as shown in Figure 2. The intercept of the line is the ratio of the heat capacities, $\Delta C_{pA} / \Delta C_{pB}$, and the slope is $\Delta C_{pA} / (m'_{pB} \Delta C_{pB})$.

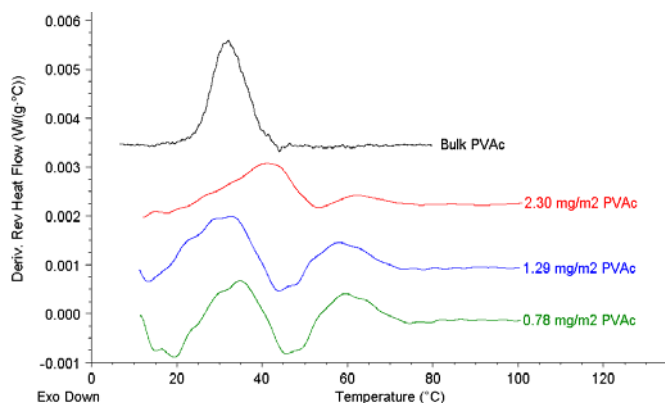


Figure 1. MDSC derivative heat flow thermograms for bulk and adsorbed PVAc on silica at different adsorbed amounts.

Table 1. Normalized Polymer Mass and Ratio of the Area of Components A and B for different Adsorbed Amounts of PVAc on Silica

Absorbed Amount (mg/m ²)	Ratio Areas of A/B (r)	Normalized Polymer Mass (m' _p)
2.30 (Hi)	7.49	0.459
1.29 (Med)	2.19	0.259
0.78 (Low)	1.70	0.156

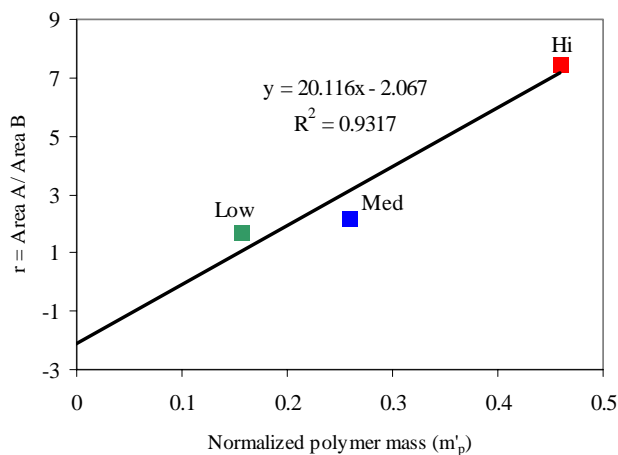


Figure 2. Ratio (r) of the areas of the A and B components of the thermograms as a function of the relative amount of polymer (m'_p).

From the preliminary data, the ratio of the heat capacities, $\Delta C_{pA}/\Delta C_{pB}$, (the intercept from the linear equation) shows the change in heat capacity of the loosely-bound component is higher than that for the tightly-bound component. This result is consistent with the result found for adsorbed PMMA,³ however, the effect does not seem to be as large. The smaller value ΔC_p for the tightly-bound component, as compared with that of the bulk polymer implies a reduction in mobility of the tightly-bound polymer above its T_g .

Conclusions

MDSC thermograms show two distinct peaks for adsorbed PVAc on silica which correspond to the loosely- and tightly-bound segments of adsorbed polymer at the interface. The relative intensities of the transitions can be used to estimate both the amount of adsorbed polymer and the ratio of the ΔC_p for both components.

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