

An AFM Study Investigating Polymers on Surfaces.

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1. Introduction

Studying polymers on surfaces can provide an insight into filler-polymer interface properties for polymer composites and nanocomposites. The polymer/carbon interface plays a major role in many polymer matrix composites. ^[1] Carbon-based particles are widely utilised in polymer composites for various applications such as; tyre rubbers (carbon black), advanced membranes (carbon nanotubes), medical equipment and superstrong construction materials (carbon fibres). ^[2-3] However, exactly why these composites have these unique properties is not fully understood at a fundamental level. ^[4]

There are a number of different techniques that could provide an insight

3. Results and Analysis

AFM provided clear images of the polymer aggregates on mica and graphite surfaces; the following results are for a styrenebutadiene random copolymer (26.3% styrene, 73.7% butadiene) with a molar mass of 85 kg/mol.



into the interface. Atomic force microscopy (AFM) can provide high resolution topography images in the nanoscale, that will show how polymers behave on a carbon/non-carbon surface. ^[5]



Figure 1. Car tyres are made of rubber reinforced by carbon black which gives the tyres high strength, robustness and durability. ^[6]

2. Experimental

Materials. Styrene-butadiene random copolymers with varying molecular weights were dispersed into toluene solutions at varying concentrations according to the polymers' overlap concentration (c^*) . The solutions were then spin coated onto either freshly cleaved mica or graphite surfaces and left to dry completely.



Figure 4. Shows the styrene butadiene polymer ($M_n = 85 kg/mol$) at various concentrations: (A) 0.001c*, (B) 0.01c*, (C) 0.1c*, and (D) 1c* on a mica surface.

Figure 5. Shows the styrene butadiene polymer ($M_n = 85 kg/mol$) at various concentrations: (A) 0.001c*, (B) 0.01c*, (C) 0.1c*, and (D) 1c* on a graphite surface.

From figure 4 and 5, it is clear that the morphology of the polymer aggregates is very different on a mica surface compared to a graphite surface. On the mica surface spherical-cap shaped nanodroplets form that increase in size with increasing concentration. The droplet shape of the polymers on the mica surface can be explained by dewetting; it is not favourable for the hydrophobic droplets to interact with the hydrophilic mica surface, therefore to reduce free energy, the chains self assemble into droplets.

At low concentrations on the graphite surface very flat, asymmetrical structures are formed, these are known as polymer "pancakes". At higher concentrations on the graphite surface continuous polymer networks are formed that get coarser as concentration is further increased. On the graphite surfaces much flatter polymer aggregates are formed, this is attributed to graphite being hydrophobic and the favourable physical interactions between the surface and the polymer.

Figure 2. Diagrams showing a polymer solution with a concentration well below, at and well above the overlap concentration of the polymer.

AFM. Images of the polymers on the graphite and mica surfaces were taken in tapping mode AFM in air. Tapping mode allows for high quality images without damaging the polymer surface.

Analysis. All analysis of AFM images was carried out on the free software Gwyddion.

Figure 6. Histogram showing the number of chains per polymer aggregate for the styrene butadiene polymer ($M_n = 85 \text{kg/mol}$) on a mica surface at a concentration of 0.001C*.

Imaging very small aggregates can provide an insight into how polymers behave at an interface. Figure 6 shows the number of chains per aggregate for the polymer on a mica surface at a concentration of 0.001c*; there are a number of very small aggregates consisting of few polymer chains.

Concentration c/c*	0.001	0.1
Average Number of Chains per Aggregate	9	4340
Average Contact Angle (Degrees)	44	26

Table 1. Showing the difference in number of chains per aggregate and contact angle for the SBR ($M_n = 85 \text{ kg/mol}$) polymer at varying concentrations on a mica surface. At 0.001C* when the polymer aggregates contain very few chains the average contact angle is larger.

4. Conclusions

The styrene butadiene random copolymer behaves very differently on mica and graphite surfaces. On mica the polymer exhibits dewetting and forms nanodroplets that increase in size with increasing concentration; this is due to absence of favourable interactions between the hydrophobic polymer and the hydrophilic surface. On the graphite surface much flatter asymmetric

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structures are formed at low concentrations, and continuous polymer networks are formed at higher concentrations. This is due to favourable interactions of the SBR with the hydrophobic graphite surface. Studying very small polymer aggregates can provide us with information on how polymers behave at an interface at the nanoscale.

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