ABSTRACT

A durable and precisely controlled interface can be constructed by means of tethered chains that connect the reinforcement to the polymer matrix. A tethered chain is an appropriately selected, functional-ended polymer chain that is chemically bonded at one end to the surface of a ceramic reinforcement (e.g., silicate glass, alumina). Its ability to extend into and mingle with the polymer matrix generates interactions at the interface that are not possible at conventional interfaces typified by van der Waals interactions alone. We have achieved a considerable understanding of the process of tethering so that it can now be exploited to construct a variety of as-designed tethered layers. These include two different chain lengths in any specified proportion, mixtures of different types of polymers, and targeted area densities of tethered chains. The variety of surfaces (and corresponding interfaces) will be described.

INTRODUCTION

It is well established by now that the presence of tethered polymer chains at the interface between two dissimilar and immiscible materials can toughen and strengthen that interface.\(^1\)\(^-\)\(^5\) It is also known that the extent of mechanical coupling and enhancement depends on such experimental variables as length, dispersity, and surface (or interface) attachment density of the polymer chains. For example, longer chains tend to have a greater benefit.\(^4\) As another example, too high a surface attachment density can actually reduce the mechanical enhancement.\(^5\) Therefore, it is important to be able to select and control chain length, dispersity, and surface attachment density. In other words, interfaces need to be tailored to get the best performance out of them in a given application.
The length of the tethered chains can be selected in advance, and functional-ended chains of the desired length synthesized or procured as starting materials. A given dispersity is difficult to obtain, since this is hard to control during polymer synthesis, and can vary widely even for batches of the same average molecular weight (chain length). The uncertainty in polymer dispersity can be overcome by using monodisperse, functional-ended chains and mixing two or three molecular weights of monodisperse chains. It should be noted, however, that monodisperse chains are expensive. The last variable, surface attachment density, must be controlled by the experimenter who is doing the tethering of the chains to the surface of the substrate.

**BACKGROUND**

Our focus is tethering from solution. That is, the substrate of interest, the surface of which contains active sites introduced in advance, is exposed to a solution of the functional-ended polymer chains of interest. A chemical reaction occurs between the functional-end of each polymer chain and an active site on the surface, leading to a chemical bond. A typical reaction is shown in Figure 1. The chemical bond attaches the polymer chain permanently and irreversibly to the surface of the solid substrate.

![Figure 1. Schematic of the chemical reaction that occurs to tether a polymer chain (PS = polystyrene) to the surface of a solid to which epoxide active sites have been introduced previously.](image)

Theory has provided a picture of the kinetics of tethering that is composed of two distinct regimes before saturation (the cessation of tethering) is reached. Theory predicts a first regime that consists of rapid tethering, at a rate controlled by rapid diffusion of the chains through the solvent to the bare surface. When the surface is fairly well covered by a layer of nonoverlapping chains, each in the expanded coil, or mushroom, conformation, tethering is predicted to slow down abruptly, starting a lengthy second regime. This slowdown, according to theory, originates in the diffusion barrier imposed by the presence of the mushroom layer to the approach of subsequent chains to the surface. As the layer gets more crowded, the tethered chains stretch away from surface to avoid lateral contact with each other in good solvent and, in doing so, become a brush. The second regime is expected to end at saturation, when a balance is reached between the energy benefit of the chemical reaction that tethers the chain ends to the
surface and the energy costs associated with stretching of the tethered chains away from surface and with entropy loss due to confinement of the chains by one end to the surface.

Experimentally, we observe three, not two, regimes of kinetics. A typical experimental run is shown in Figure 2. The first, and part of the second, regime observed in our experimental studies starts out in qualitative agreement with theory. However, after some time, experiment veers dramatically from theory, as the second regime is interrupted by a sudden acceleration in the tethering rate. The acceleration, which continues until saturation is reached, is a distinct third regime. A significant increase in surface attachment density takes place during the third regime as compared with a nearly negligible increase during the second regime. This suggests that the transition from mushroom layer to brush takes place in the relatively short third regime, rather than occurring more slowly and gradually in a lengthy second regime. To explain the existence of the third regime, we proposed a mechanism based on random sequential tethering of deformable chains. A Monte Carlo simulation of this mechanism yielded the observed acceleration in tethering rate.

![Figure 2](image-url)

Figure 2. Typical plot of tethered chain density on surface versus time in good solvent for polystyrene of $M_n = 4,000$. The three regimes, separated by vertical lines, are labeled. Note change from linear to log scale at 60 min on x-axis.
Tethering experiments run at different temperatures, in different good solvents, and with different molecular weights of functional-ended polymer, have all shown the three-regime kinetics. Thus such kinetics can be regarded as general when tethering is done in good solvent. The advantage of the distinct regimes of kinetics is a practical one. The changes in rate that separate the regimes can be used as processing benchmarks for control of the tethered layer. For example, the sudden slowdown that ends the first regime marks the point in time when the mushroom layer has been completed. The slow second regime is a window of opportunity for adding chains of another length or another type, or of switching polymer solutions completely. Finally, the acceleration that marks the onset of the third regime also reminds the experimenter that saturation has not been reached and that more time is required.

EXPERIMENTAL

Preparation of Solid Substrate and Introduction of Active Sites

The solid substrate to which the above functional-ended polymer chains were tethered was silicate glass in the form of nonporous, spherical beads (Potters Industries, Cleveland, OH). These beads had an average specific surface area of 0.24 m²/g. They were cleaned with piranha solution and dried before use. Epoxide functional groups for subsequent reaction with the amine functional ends of the polystyrene chains were introduced to the surface of the beads by exposure to 3-glycidoxypropyltrimethoxysilane (98%, Aldrich, Minneapolis, MN) in toluene under anhydrous conditions. This resulted in $2.71 \pm 0.24$ epoxide groups/nm² of glass surface, a surface density value well above that needed for tethering of polymer chains at the highest conceivable surface density.4

Tethering Reactions

Reactions in Good Solvent. All tethering reactions were run at room temperature, under argon atmosphere, with functional-ended, monodisperse polystyrene chains of various molecular weights, provided by Prof. R. P. Quirk, University of Akron. The glassware that had been previously treated with n-butyl-trichlorosilane (an effective surface energy reducer) to prevent segmental adsorption of polystyrene to the glassware. In a typical tethering reaction in good solvent, the reaction flask was charged with 20 mL of reagent grade toluene into which was dissolved 0.0051 g of functional-ended polystyrene of the desired $M_n$. This solution was spiked with a carefully weighed amount of internal standard for use in the quantitative analysis, described below, of the tethering process. As internal standard, mono-disperse polystyrene, purchased as a molecular weight standard from Polymer Standards Service, Silver Spring, MD, was used. The inert chain-ends rendered it incapable of participating in the
tethering reaction. Furthermore, because it was available in many different molecular weights, we could choose a molecular weight whose peak is size exclusion chromatography did not overlap that of the functional-ended polystyrene. Before the solid substrate was added to the reaction vessel, two or three aliquots of the solution were subjected to size exclusion chromatography to establish the peak area ratio for functional-ended polymer to internal standard at zero time. (Mass ratio was known from the initial weighing operation.) Then, 18.1 g of surface-derivatized glass beads were added to the flask, and the tethering process began immediately. It was our usual practice to run each tethering reaction in duplicate, i.e., two separate but identical reactions run simultaneously in separate flasks, for confirmation of reproducibility. This practice also provided a back-up in case of a laboratory mishap during these week-long reactions.

Auxiliary experiments were done to confirm the absence of segmental adsorption of polystyrene in toluene to derivatized glass beads and to the glassware. These experiments consisted of exposure of the derivatized beads (or the glassware) to solutions containing inert-ended polymer of two different molecular weights. The mass ratio of the two molecular weights in solution is a sensitive indicator of adsorption, since polymer chains of low molecular weight absorb fastest at early times and are displaced by chains of high molecular weight at long times. Adsorption would be indicated by a changing ratio. Analyses of the solutions showed that both absolute and relative values of the two molecular weights remained constant, verifying the absence of segmental adsorption to either the derivatized beads or the glassware.

**Tethering Reactions in Poor Solvent.** The tethering reactions in poor solvent were run in the same way as those in good solvent, except for a few essential details. First, reagent grade cyclohexane was used as the solvent instead of toluene. Second, although the tethering reactions were run in duplicate as above, the two reactions in each pair two differed from each other in that one was spiked with monodisperse, inert-ended polystyrene as the internal standard, while the other was spiked with monodisperse polyisoprene as the internal standard. Polyisoprene, purchased as a molecular weight standard from Polymer Standards Service, Silver Spring MD, was not expected to exhibit segmental adsorption from cyclohexane, since the latter is a good solvent for the former. The absence of detectable adsorption of polyisoprene onto either the glassware or the derivatized glass beads was confirmed by auxiliary experiments in cyclohexane similar to those described above for polystyrene in toluene.
Monitoring the Tethering Reactions

Reactions run in good solvent. Representative aliquots, containing glass beads as well as polymer solution, were removed from the stirring reaction mixture at frequent intervals for quantitative analysis of chains remaining in solution. Immediately after removal from the reaction vessel, each aliquot was treated with excess trichloroacetyl isocyanate to quench the tethering reaction by capping the functional end of each polymer chain. Next, the beads were removed from the aliquot by means of a syringe filter, leaving behind a clear solution that contained the chains not yet tethered and the internal standard. This solution was analyzed by means of size exclusion chromatography on a Waters LC system (Waters Corp., Milford, MA) equipped with two Styragel columns and ultraviolet and refractive index detectors. From the chromatogram, the mass of functional-ended polystyrene remaining in solution was determined relative to that of the internal standard by comparison of peak areas. Relative peak area at sampling time, \( t \), was normalized by relative peak area at \( t = 0 \) (before addition of beads) to yield mass fraction in solution at time, \( t \). The mass tethered was determined by difference between the mass in solution at \( t = 0 \) and sampling time, \( t \). Mass tethered was converted to number of chains tethered by use of the known value of \( M_n \), and division by the total surface area of the substrate yielded surface attachment density, chains/nm\(^2\).

Reactions run in poor solvent. At frequent intervals, representative aliquots were removed from the duplicate stirring reaction mixtures and were immediately quenched with excess trichloroacetyl isocyanate, as described above. After quenching, the aliquots removed from reactions containing polystyrene as internal standard and from those containing polyisoprene as internal standard were treated differently. In the case of the aliquots containing polystyrene as internal standard, the cyclohexane was evaporated and was replaced with an equal amount of toluene. The purpose of the toluene was to desorb any of the polystyrene internal standard and nontethered, functional-ended polystyrene from the beads. Then the beads, containing only tethered chains, were removed from the aliquot by means of a syringe filter, and the clear toluene solution was analyzed by size exclusion chromatography. From the chromatogram, the mass fraction of functional-ended polystyrene chains remaining in solution was determined as described above, and the number of chains tethered (chemically bonded) to the surface of the substrate at the time the aliquot was taken was computed by difference. Aliquots from reactions containing polyisoprene as the internal standard were used for determination of the sum of tethered and adsorbed functional-ended polystyrene chains. Separation of the beads from the quenched aliquot left a clear solution containing the polyisoprene internal standard plus only the functional-ended polystyrene that remained completely free in the cyclohexane solvent. Tethered or adsorbed chains were removed
with the beads. The bead-free solution was analyzed by size exclusion chromatography, and the mass fraction of functional-ended polystyrene chains remaining in solution (neither tethered nor adsorbed) was determined with reference to \( t = 0 \), as described above. The sum of functional-ended polystyrene chains adsorbed and tethered at the time the aliquot was taken was computed by difference.

At any given time, the number of chains adsorbed was taken to be the difference between results obtained from analysis of aliquots removed from reactions containing inert-ended polystyrene as internal standard and results obtained from analysis of aliquots removed from reactions containing polyisoprene as internal standard.

**RESULTS AND DISCUSSION**

Table 1 presents results of experiments in which polymer chains of different molecular weights were tethered separately, and each reaction was allowed to go to saturation. \( M_n \) in the table is number average molecular weight in grams/mole. Values for surface attachment density for mushroom and brush layers are presented. Two interesting features emerge from the table. First, for each molecular weight, the brush layer (evaluated at saturation) is much more dense than the mushroom layer. Second, the surface attachment density is inversely related to molecular weight of the tethered polymer chains.

Table 1. Values for Surface Attachment Density

<table>
<thead>
<tr>
<th>( M_n )</th>
<th>( \text{Chains/} \text{nm}^2, \text{mushroom} )</th>
<th>( \text{Chains/} \text{nm}^2, \text{brush} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000</td>
<td>0.014</td>
<td>0.070</td>
</tr>
<tr>
<td>15,000</td>
<td>0.0094</td>
<td>0.024</td>
</tr>
<tr>
<td>44,000</td>
<td>0.0024</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

Table 2 presents results of experiments in which polymer chains of different molecular weights were tethered from the same solution simultaneously. Again, each tethering reaction was allowed to go to saturation. Since the final layer is mixed, only the values for surface attachment density at saturation are reported. From Table 2, it is clear that the short chains always have an advantage over long chains because of their faster diffusion rate through solution and through the already tethered layer.
Table 2. Surface Attachment Densities for Tethering from Solution Containing Two Molecular Weights, \(M_n = 4,000\) (Short) and 44,000 (Long).

<table>
<thead>
<tr>
<th>Initial ratio, short to long, in solution</th>
<th>Short chains/(\text{nm}^2) in tethered layer</th>
<th>Long chains/(\text{nm}^2) in tethered layer</th>
<th>Final ratio, short to long, in tethered layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 to 1</td>
<td>0.070</td>
<td>0.0019</td>
<td>36 to 1</td>
</tr>
<tr>
<td>2.2 to 1</td>
<td>0.051</td>
<td>0.012</td>
<td>4.7 to 1</td>
</tr>
</tbody>
</table>

Table 3 presents results of experiments in which polymer chains of different molecular weights were tethered separately to the same surface. This was accomplished by switching solutions after tethering from the first solution (of a single molecular weight) had reached the process window offered by the second regime. The tethering reaction involving the second solution (containing a single molecular weight, but different from the first) was then allowed to go to saturation.

Table 3. Surface Attachment Densities for Sequential Tethering of Two Molecular Weights, \(M_n = 4,000\) (Short) and 44,000 (Long).

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Short chains/(\text{nm}^2) in tethered layer</th>
<th>Long chains/(\text{nm}^2) in tethered layer</th>
<th>Final ratio, short to long, in tethered layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short to mushroom, then long to saturation</td>
<td>0.018</td>
<td>0.0042</td>
<td>to 1</td>
</tr>
<tr>
<td>Long to mushroom, then short to saturation</td>
<td>0.046</td>
<td>0.0016</td>
<td>to 1</td>
</tr>
</tbody>
</table>

Table 4 presents a comparison of the surface attachment density achieved by changing from good to poor solvent. As can be seen, the tethering density is nearly doubled by the use of a poor solvent. This is due to the fact that segmental adsorption, which does not occur in tethering reactions conducted in good solvent, does occur in poor solvent. Such segmental adsorption enhances the final tethering density.

Table 4. Surface Attachment Densities at Saturation for Tethering from Good Solvent Versus Poor Solvent.

<table>
<thead>
<tr>
<th>(M_n)</th>
<th>Chains/(\text{nm}^2) in good solvent</th>
<th>Chains/(\text{nm}^2) in poor solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000</td>
<td>0.070</td>
<td>0.11</td>
</tr>
<tr>
<td>44,000</td>
<td>0.0056</td>
<td>0.0098</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Tethering of polymer chains from good solvent to a substrate displays three distinct regimes of kinetics. The experimenter can exploit these regimes to construct diverse tethered layers. Surface attachment density of polymer chains of a single molecular weight can be controlled. Tethered layers of mixed molecular weights can be constructed, and the relative amounts of the molecular weights can be controlled to some extent. The construction of mixed layers can be approached by means of tethering simultaneously from a solution that contains both polymers, or can be approached by switching polymers in the middle of the tethering reactions. Finally, surface attachment density can be increased by tethering from poor solvent instead of from good solvent.

REFERENCES