Soft Matter

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Journal:	*Soft Matter*
Manuscript ID	SM-COM-12-2021-001833.R1
Article Type:	Communication
Date Submitted by the Author:	23-Mar-2022
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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Adhesion is a molecular event where polymer chains contact with a material surface to form an interfacial layer. To obtain a better understanding of the adhesion on a molecular scale, we herein examined the conformational change of polystyrene (PS) chains at the film surface after contacting with hydrophobic or hydrophilic surfaces using sum-frequency generation (SFG) spectroscopy. Chains altered their local conformations with a quartz surface more quickly than a hydrophobic alkyl-functionalized one. A full-atomistic molecular dynamics simulation showed that these results, which were coupled with the contact process of PS chains with the solid surface, could be explained in terms of the Coulomb interaction between them.

Hot melt adhesive is a class of thermoplastic materials that functions when it is solidified at the surface of the adherend, and is used in a wide range of applications.[1, 2] From the viewpoint of the molecular scale, adhesion is a process whereby polymer chains are frozen in contact with the adherend surface. Thus, it is expected that chains first contact with the adherend surface and then alter their local conformations to minimize the free energy at the interface, leading to the chain adsorption to the adherend surface. This hypothesis is well consistent with our experience in daily life where the effectiveness of an adhesive is strongly dependent on the quality of the adherend surface. The objective of this study was to provide direct support for this hypothesis, if any, by the interfacial sensitive technique of sum-frequency generation (SFG) spectroscopy[3, 4] in conjunction with a full-atomistic molecular dynamics (MD) simulation. Our model experiment comprised a polystyrene (PS) film which was heated to a temperature between the glass transition temperatures (T_g) at the surface and in the bulk, onto which a solid substance was then mounted. That is, PS and the solid were regarded as adhesive and adherend, respectively. Although the static orientation of PS phenyl groups at solid interfaces has been studied using SFG[5, 6] and MD simulation[7], it remains unclear how the local conformation dynamically alters in response to the change in the contact medium from the air to the adherend.

In general, the aggregation states and thermal molecular motion of polymer chains at the surface[8-12] and interfaces[13-17] are different from those in the corresponding bulk state. For example, certain functional groups are preferentially oriented at the surface[18] as well as the interfaces[19-22] due to the free energy minimization even in a homo-polymer system. Also, there exists a mobility gradient in the surface region; the segmental dynamics being faster at the surface than in the bulk.[23-25] Although the reasons for this are still controversial, lesser cooperativity is definitely one of them.[23] On the other hand, the segmental mobility becomes slower in close proximity to the interface with a solid.[26] It should be noted that these established phenomena are involved in the experiments conducted in this study.

As a model polymer, monodisperse PS (Polymer Source Inc., Dorval, Quebec, Canada) with a number-average molecular weight (M_n) of 28k and a molecular weight distribution (PDI) of 1.06 was used. The bulk T_g was 374 K by differential scanning calorimetry. The surface T_g was estimated to be 295 K on the basis of our previous study.[23] PS films with a thickness of ca. 200 nm were prepared by a spin-coating method from a toluene solution onto half-cylindrical quartz prisms. They were annealed under vacuum at 423 K, being higher than the bulk T_g, for 12 h. To prepare a hydrophobic adherent, a quartz window was first cleaned by a piranha solution (a mixture of 3:1 (v/v) 98% H_2SO_4 and 30% H_2O_2 in water) at 373 K for 2 h and then functionalized by octyldimethyl chlorosilane (ODS) based on chemical vapor deposition. Also, a quartz window just cleaned by the procedure was used as a hydrophilic adherent. The surface free energy for the PS film, the ODS and quartz substrates were estimated to be 42.4±0.3, 30.2±1.3, and 62.3±0.9 mJ•m^{-2}, respectively, following Owens' method with water and diiodemethane as probe liquids.[27]

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The local conformation of PS chains before and after attaching to either the hydrophobic or hydrophilic surface was examined by SFG measurement (EKSPLA, Vilnius, Lithuania), in which a visible beam with a wavelength of 532 nm and a tunable infrared (IR) beam were introduced to a specimen from the prism side with incident angles of 65° and 55° relative to the substrate normal, respectively. The analytical depth of SFG is the best among available techniques and is sub-nanometer scale.[4] The measurements were carried out using the *ssp* (SFG/*s*; visible/*s*; and IR/*p*) polarization combination, meaning that the vibrational information along the direction normal to the interface was obtained. The power of visible and IR beams was adjusted as low as possible to prevent the sample damage. Spectroscopic measurements confirmed that the samples were not damaged after the measurements. Figure 1(a) shows the sample geometry. The ODS or quartz surface kept at 363 K, which was between the surface and bulk T_gs of PS, was attached to the PS film prepared on a quartz prism. This temperature was chosen because the spectrum remained unchanged at room temperature below the surface T_g.

MD simulations were performed to better understand the contact process of PS segments onto the solid surface using the Materials Studio 2021 (Dassault Systèmes) software package with the Forcite module and the COMPASS III force field.[28] Ten 100-mer PS chains were packed into a unit cell with a size of 5.1×5.4×15.0 nm^3 and a density of 1.06 g·cm^{-3}, and the MD simulation of 1 ns was conducted at 393 K and 1 atm under an NPT ensemble to relax the structure. After the top and bottom of the cell were opened to create the free surface, nitrogen molecules were inserted in the top and bottom spaces so that the pressure could be 1 atm and then the layered structure of PS chains was relaxed. Then, using the layered structure of quartz, the ethyl- and OH-terminated surfaces were created for the model ODS and quartz, respectively. The PS model was placed at a position slightly away from the model adherend surface to fabricate the initial structure. MD simulations were then performed for 2 ns at 298 K.

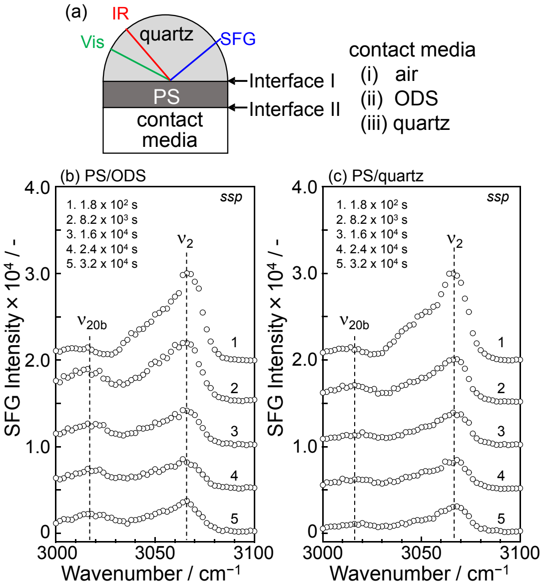

Figure 1. (a) Schematic representation of the sample geometry in this study. SFG spectra with the *ssp* polarization combination for PS films attaching to (b) ODS surface and (c) quartz surface, as a function of time.

Figure 1(b) shows SFG spectra in the aromatic C-H vibration region for a PS film attaching to the ODS surface. Here the signal intensity was divided by the intensity of incident visible and IR. Each spectrum has been vertically shifted for clarity. Peaks were observed at 3,018 and 3,066 cm^{-1} which were assignable to the ν_{20b} and ν_2 modes for phenyl groups of PS.[6, 18] To obtain SFG signals from functional groups, the centrosymmetry must be broken. Such a condition can be generally satisfied by ordering functional groups at interfaces. Thus, the spectrum reflects that phenyl groups were aligned at interfaces.

Panels (b) and (c) of Figure 1 show SFG spectra for PS films after attaching to ODS and quartz surfaces, respectively, as a function of time. The signal intensity is proportional to the number density and the orientation of functional groups. Postulating that the population of the functional groups remained unchanged, the change in signal intensity with time can be assigned to the orientational relaxation of the functional groups, which is attained by the change in local conformation of chains. The Fresnel coefficients for the interfaces I and II were roughly calculated to be 0.50 and 0.60, respectively.[29] This means that the SFG signals were comparably generated from at the interfaces I and II. However, postulating that the local conformation of chains at the interface I is the same in the two systems, the spectral difference, or the signal intensity difference, between the two systems can be attributed to the conformational difference of chains at the ODS and quartz surfaces. For both cases, the signal intensity became weaker at 8.2 x 10^3 s. The decrement of the signal intensity from PS was more remarkable on quartz than on ODS. In addition, the SFG signals kept decreasing with increasing time. These make it clear that the orientational relaxation for phenyl groups of PS upon contacting the solid surface proceeded even at 363 K, being higher than and lower than the surface and bulk T_gs, respectively.

To discuss the kinetics of conformational change for PS at the interface, the normalized signal intensity of the ν_2 mode ($I_{\nu 2}$) was analyzed as a function of time. Figure 2 shows the time course of $I_{\nu 2}$ for the PS/ODS and PS/quartz, respectively. Data represented by open symbols were continuously acquired as a function of time at 3,066 cm^{-1}. On the other hand, data by filled symbols were imported from spectra shown in Figure 1. They were taken from the same sample by switching the measurement mode. Here, the signal intensity was normalized by the intensity of the spectrum obtained after the contact (t = 1.8 x 10^2 s). As a general trend, the $I_{\nu 2}$ remained unchanged for a short while and then started to decrease with increasing time. In the case of the PS/ODS, it started to decrease at around 3.6 x 10^3 s. However, it reached a plateau once the time went beyond 1.9 × 10^4 s. On the other hand, the $I_{\nu 2}$ for the PS/quartz started to decrease at around 1.4 x 10^3 s and kept decreasing within the measurement time range employed. This indicates that the conformational change occurred more quickly at the quartz surface than at the ODS one. In addition, the extent was more significant for the quartz surface.

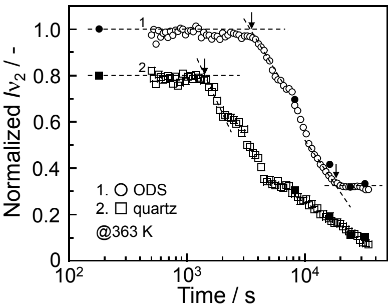

Figure 2. Time dependence of normalized SFG intensity for the ν_2 mode of PS at 363 K after attaching to the ODS and quartz adherends. Filled symbols denote the values obtained from Figure 1 (b) and (c). Broken lines denote guides for the eye.

Before attaching to the adherend, the PS film had a free surface in which the segmental mobility was enhanced in comparison with the internal bulk region. Thus, even at 363 K, PS chains in the outermost region of the film could change their conformations to fit into place, which was now the interface with the adherend. The greater the surface free energy of the adherend, the more remarkable the conformational change of PS. Thus, the $I_{\nu 2}$ decrement, resulting from the conformational change, became more remarkable for PS at the quartz interface. The feature of surface mobility disappeared with increasing time due to the development of the adherend-interfacial layer, and instead, the feature of interfacial mobility which was less active than that in the bulk appeared. This means that the reorganization of chains in the interfacial region eventually decelerated. This behavior could be clearly observed for the PS/ODS interface. Besides, the $I_{\nu 2}$ did not reach zero within the time scale used. Hence, it seems most likely that PS chains at the interfacial region somehow maintained their orientation at the interface even after reaching the apparent plateau reagion.[20]

When a solid matter attaches to the PS film, it is hard to form a close contact between the two surfaces due to the surface roughness, as often claimed in discussions of frictional properties.[30] This problem might have affected the above SFG measurements. In addition, the MD simulation which enables us to gain direct access to the information of orientation for phenyl groups at the interfaces can be difficult to conduct because of the difficulty of constructing an appropriate initial structure for the system. Such a situation limits our MD simulations to a qualitative assessment. Once the PS surface was attached to the adherend surface and vice-versa, PS segments started to contact to the adherend surface. This process was faster onto the quartz than onto the ODS surface. The polarizability of the model ODS surface was small, and the charges of hydrogen and carbon atoms on the surface were +0.05*e* and -0.16*e*, respectively. Those of hydrogen and oxygen atoms on the quartz surface were +0.25*e* and -0.47*e*, respectively. Also, on the PS surface, phenyl rings faced to the solid surface, and the charges of hydrogen and carbon atoms were -0.13*e* and +0.13*e*, respectively. Thus, it can be claimed that the contact of PS segments was faster onto the quartz surface due to the larger surface charge. This hypothesis was evidenced by another finding that as the surface charge of the quartz set to zero, the interfacial reorganization was slowed down to the same degree as onto the ODS surface. Of course, during the contact process, PS segments are supposed to alter the local conformation. This picture is consistent with the results shown in Figure 2.

Similar experiments were performed with poly(*n*-butyl methacrylate) (PnBMA) (M_n = 17.5k , PDI = 1.04, bulk T_g = 310 K) to verify the universality of this phenomenon. PnBMA has polar ester groups at the base of the side chain parts and is often used as one of the main ingredients of the pressure sensitive adhesive. The orientational relaxation of methyl groups at the terminus of ester butyl side chains was observed at both ODS and quartz interfaces at room temperature. This means that after contacting the PnBMA film with a solid surface, chains in the outermost region of the film changed their local conformation. This is in good accordance with the results using PS. However, the rate of the interfacial reorganization was quite similar to the both interfaces, and the MD simulation also gave the same conclusion. At a glance, this result seems to be hardly explained only in terms of the surface charge.

The charges of hydrogen and carbon atoms for a methyl group at the end of a butyl group for PnBMA was +0.05*e* and -0.16*e*, respectively. Since only hydrogen atoms of methyl groups directly interacted with the surface, carbon atoms were shielded from the substrate. This is contrast to the case of PS, where phenyl rings lied directly down on the adherend surface and thereby both hydrogen and carbon atoms of phenyl groups were involved in the interaction with the surface. Thus, in the case of PnBMA, the effect of the Coulomb interaction with the surface on the orientational relaxation of the methyl groups became quite weak. Consequently, the relaxation kinetics of the interfacial local conformation for PnBMA was almost the same on ODS and quartz surfaces. A conclusive study on this issue will be reported in the near future.

Conclusions

The conformational change of PS chains on a solid surface was examined by SFG in conjunction with MD. The SFG measurements revealed that PS chains became randomized at the adherend interface as long as the temperature was higher than the surface T_g and the kinetics was faster at the quartz interface than at the ODS interface. However, the process appeared somewhat complicated because it contained the surface and interfacial dynamics of polymer chains which were faster and slower than the corresponding bulk one, respectively. The MD simulation made it clear that the contact process of PS chains to the adherend surface, and thereby the kinetics of the conformational change at the interface, was dependent on the Coulomb interaction between them. Based on these results, it seems reasonable to imply that once a hot melt adhesive is applied to the adherend surface, polymer chains change the conformation to minimize the interfacial energy and lose their mobility with decreasing temperature. In other words, the chemical quality of the adherend surface strongly impacts the strength of the adhesives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by JSPS KAKENHI for Scientific Research (B) (No. JP20H02790) to KT and Scientific Research (B) (No. JP20H02802) to DK from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan. We are also thankful for the support from the JST-Mirai Program (JPMJMI18A2) (K.T.).

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