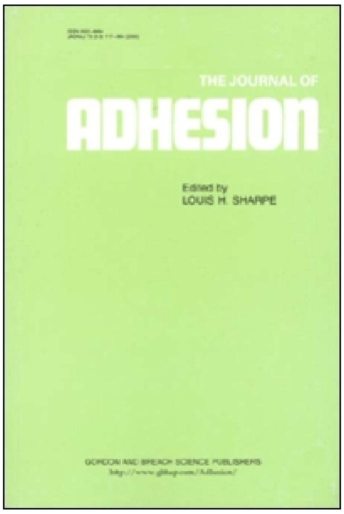
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion Frequency in Interfacial Dynamics of Copolymers

L. Ll[a]; B. Abedian[a]
[a] Department of Mechanical Engineering, Tufts University, Medford, MA, USA

To cite this Article Ll, L. and Abedian, B.(2001) 'Adhesion Frequency in Interfacial Dynamics of Copolymers', The Journal of Adhesion, 75: 3, 325 — 340
To link to this Article: DOI: 10.1080/00218460108029607
URL: http://dx.doi.org/10.1080/00218460108029607

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 2001, Vol. 75, pp. 325–340
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.

Adhesion Frequency in Interfacial Dynamics of Copolymers*

L. LI and B. ABEDIAN[†]

Department of Mechanical Engineering, Tufts University, Medford, MA 02155, USA

(Received 13 May 2000; In final form 5 October 2000)

This paper introduces the concept of *adhesion frequency* that characterizes the dynamic interaction between a polymer matrix and a solid surface. It is argued that the pressure sensitive bonding of a polymer interface occurs within a critical time scale below which no wetting is established upon contact. The adhesion frequency can be viewed as the inverse of this critical time scale. The bonding kinetics is used to model transient adhesion and take into account the growth of bonding energy with time. The mechanics of the interfacial dynamics is used to derive expressions for the adhesion frequency when inertial, viscous or elastic effects dominate the surface deformation. Transient adhesion effects are also investigated experimentally using non-axisymmetric rotating bits and commercially-available copolymer adhesives. The rotating bits induce an oscillatory motion on the polymer surface. Experiments are conducted with the rotating bits spinning at a wide range of speeds making it possible to obtain the dynamic response of the polymer interface as well as to measure the adhesion frequency for the tested polymers.

Keywords: Pressure sensitive adhesive; Polymer interface; Copolymer bonding; Adhesion frequency; Wetting dynamics; Rotating bit

INTRODUCTION

An adhesive bond occurs when the high-energy, reactive surface of a polymer-matrix composite is brought into contact with a solid surface.

---

*Presented at the 23rd Annual Meeting of The Adhesion Society, Inc., Myrtle Beach, South Carolina, USA, February 20–23, 2000.

[†]Corresponding author. Tel.: 617-627-3012, Fax: 617-627-3058, e-mail: babedian@tufts.edu

During the bonding interaction, the polymers at the free surface of the composite matrix undergo a realignment transition to an adsorbed state through a molecular organizational hierarchy at the polymer-solid interface [1]. The transient adhesion phenomenon becomes dynamic when there is a relative motion between the bulk of a polymer matrix and a solid surface. Under a dynamic condition, the interfacial bonding energy competes with the required energy for deformation of the free surface of the polymer matrix, setting the stage for conditions under which no wetting occurs if the time is short enough such that the deformational energy surpasses the bonding energy. Accordingly, by vibrating the free surface of the polymer beyond a certain frequency, the adhesion frequency, interactions of the solid surface and the polymer occur in the absence of an adhesive bond. The adhesion frequency is an interfacial parameter and depends on transient adhesion characteristics at the interface as well as viscoelastic properties of the polymer matrix.

From a process point of view in industrial and biomedical applications, such as mold release and restoration practice in dentistry, there are instances in which it is desirable to suppress this bonding phenomenon. This interfacial effect is discussed in light of the development of a new method of handling polymer-matrix composites in applications [2]. This method involves vibration of the solid-polymer interface at different frequencies. For each solid-polymer combination, there is an adhesion frequency at which the sum of the viscoelastic and inertial energies of the fluid at the surface exceeds the energy available for bonding. When the polymer is vibrated at or beyond this frequency, the adhesive matrix can be deformed without adhesion. An important aspect of the developed process is that it can be used to characterize surface and interfacial properties of polymers under dynamic conditions, whereas existing techniques are restricted to the study of bulk dynamic properties.

Polymeric composites can be classified into two different categories: high-viscosity formulations and low-viscosity "flowable" composites. The difference in viscosity between the two classes is often caused by differences in filler particle content and size. The flowable materials are currently preferred in some processes, because they can be directly applied into an area with no further adjustments required. The high-viscosity materials, on the other hand, may need to be manipulated with an instrument in order to ensure adaptation to the bonding walls. This is seen as a disadvantage, because these materials are highly adhesive and difficult to manipulate. This difficulty can introduce defects such as voids and air pockets into the adhesive material in the final cured state. Such defects may cause degradation of nominal mechanical properties. The advantage of the high-viscosity materials is that because of their higher filler content, their mechanical properties are significantly better than those of the flowable materials. The technology exists to manufacture high-viscosity composites with very favorable mechanical properties; they are not manufactured, however, because the difficulty in manipulating these materials with conventional means renders them virtually unworkable in applications.

The focus of this work is to determine dynamic conditions under which the adhesive bond can be avoided. In the experiments, we induce interfacial oscillations at the solid–liquid interface of prepared polymer samples using rotating bits with non-axisymmetric cross sections. For different bit geometries, the rotating bits are inserted in a prepared polymer sample using a computer-controlled setup. The interaction of the rotating bit and the polymer matrix is detected by measuring the instantaneous force experienced by the bit during insertion/extraction cycles. The interfacial behavior is also captured using a computer-based imaging system. The tests are performed for five commercially-available composite materials primarily made of bisphenol A-glycidyl methacrylate (BIS-GMA) and triethylene glycol dimethacrylate (TEGDMA). The experiments were repeated for different rotational speed of the bits. The results indicate that for each tested material there is a maximum frequency above which there is no adhesive bonding between the polymer matrix and the rotating bit.

The wetting dynamics is also treated theoretically when the adhesive interface undergoes a sinusoidal oscillation. It is argued that dynamic bonding of a polymer interface can occur when the bonding energy is larger than the energy required for the oscillatory motion of the polymeric interface. It is shown that an expression for the minimum frequency can be derived depending upon whether the inertial, viscous or elastic effect is dominant in the interfacial dynamics.

THEORY

For a liquid on a solid surface, the interfacial equilibrium is expressed in terms of the work of adhesion, W_a, for formation of the interface [3].

$$W_a = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta} \tag{1}$$

where γ_α is the surface tension of phase α, γ_β the surface tension of phase β, and $\gamma_{\alpha\beta}$ the interfacial tension between phases α and β. W_a is a reversible work.

Dynamic adhesion can be characterized quantitatively as the total bond energy, θ, dissipated during debonding of the solid–liquid interface. Quantitative pressure-sensitive adhesion measurements can be performed by determining the force necessary to debond an adhesive fluid from a solid surface [4, 5]. The total adhesion energy, θ, is expressed as a product of the reversible work of adsorption, θ_o, and the irreversible work of deformation of the adhesive, H.

$$\theta = \theta_o H. \tag{2}$$

θ_o is related to the activation energy per unit area of wetted surface [6]. In the limit of slow rate of change,

$$H \rightarrow 1 \quad \text{as} \quad t \rightarrow \infty \tag{3}$$

The kinetics of adhesive bond formation in polymeric liquids has been reviewed by Wu [7]. The rate of spontaneous wetting can be modeled in terms of a first-order equation for instantaneous contact angle, θ_c, and the interfacial area at time t [8]. Let us assume that the adhesive bond strength, σ_f, is proportional to the effective wetted area, A. Macromolecules in the proximity of the solid surface will form an adhesive bond through diffusional effects. Linear diffusion propagates according to $t^{1/2}$ and the rate of change of wetted area will then be proportional to t along with the total wetted area, A. In differential form, the change of area can be written as

$$dA = kAdt \tag{4}$$

where k is a rate constant. Making use of the proportionality between the wetted area and the adhesive bond strength, σ_f, and assuming no bonding at the initial contact time, the expression for σ_f will be

$$\frac{\sigma_f}{\sigma_f^{\infty}} = 1 - e^{-t/\tau} \tag{5}$$

where σ_f^{∞} is the adhesive bond strength at infinite time and τ is the retardation time constant. τ can be related to temperature using an Arrhenius-type equation. Equation (5) agrees well with experimental data for a rubber adhesive on gold [9]. This equation indicates that σ_f varies linearly with time for $t \ll \tau$; consequently, the shorter the time of contact between fluid and solid, the weaker the adhesive bond. Consequently, the adhesive bond is inversely proportional to the induced interfacial frequency at the adhesive surface.

Also, as the oscillation frequency increases, the rate of strain at the fluid surface increases. For a strain $\varepsilon(t)$ at the fluid surface, the viscoelastic and inertial stresses, expressed as τ_{visc} and τ_{in}, respectively, are given by [10]

$$\tau_{\text{visc}} = E_b\varepsilon(t) + (\eta_b + \eta_s)\frac{d\varepsilon}{dt} \tag{6}$$

and

$$\tau_{\text{in}} = \rho a \frac{d^2\varepsilon}{dt^2} \tag{7}$$

where E_b is the bulk modulus of elasticity, η_b is the bulk viscosity of the viscoelastic fluid, η_s represents the surface viscosity [10], ρ is the fluid density, and a is the length scale that characterizes the deformation of the surface. η_b encompasses dissipative and non-dissipative portions of the complex viscosity. Depending on the frequency range, it increases with the oscillation frequency according to a square or a square-root law [11]. In the limit of high frequencies induced at the interface, the dissipative portion of the dynamic viscosity dominates viscoelastic behavior of the matrix.

With the free surface moving with a velocity $a(d\varepsilon/dt)$, the change in energy due to dynamic deformation of the surface takes the following form,

$$\frac{dE}{dt} = \frac{1}{2}E_b\frac{d\varepsilon^2}{dt} + (\eta_b + \eta_s)\left(\frac{d\varepsilon}{dt}\right)^2 + \frac{1}{2}\rho a\frac{d}{dt}\left(\left(\frac{d\varepsilon}{dt}\right)^2\right) \tag{8}$$

If it is assumed that the fluid surface undergoes a periodic sinusoidal deformation,

$$\varepsilon(t) = \varepsilon_o \sin(\omega t), \tag{9}$$

Equation (8) becomes

$$|\Delta E| = \frac{1}{2} E_b \varepsilon_o^2 \omega + [\eta_b(\omega) + \eta_s] \omega^2 \varepsilon_o^2 + \frac{1}{2} \rho a \omega^3 \varepsilon_o^2 \tag{10}$$

Equation (10) represents the amount of time-averaged excess energy required for pressure-sensitive adhesion to take place, if the fluid surface undergoes a sinusoidal oscillation. Equations (9) and (10) show that increasing the deformation frequency increases the viscoelastic and inertial energies of the fluid at the surface.

Accordingly, raising the energy required for the solid–fluid interface to form the bond can prevent bonding in a pressure-sensitive adhesion. This can be accomplished by subjecting the fluid at the interface to a periodic deformation. For example, inserting a rotating probe that is non-axisymmetric or has periodic protrusions on its cross-section would accomplish this. An example of such an instrument has been provided elsewhere [2].

One might also conclude further that there exists an adhesion frequency at which the sum of the viscoelastic and inertial energies of the fluid exceeds the available energy for adsorption for a given fluid–solid interface system. The *adhesion frequency* ω_c represents the minimum oscillation of the interface for prevention of the bond between the adhesive and the approaching solid surface.

No general solution for ω_c can be obtained from Eq. (10), particularly in view of the fact that dependency of polymer viscosity on frequency varies in different frequency ranges. Yet, when the frequency is high enough, the inertia term will be dominant among the terms on the right-hand side of Eq. (10). This, in particular, can be the case for composites with a high concentration of filler particles. Thus, neglecting the viscoelastic terms, Eq. (10) can be rearranged to obtain an expression for the characteristic frequency, ω_c, for the inertia-dominated case.

$$\omega_c = \left(\frac{2\Delta E_o}{\rho a \varepsilon_o^2 \tau} \right)^{1/4} \tag{11}$$

Here we have used the high-frequency limit of Eq. (5) in the form

$$\Delta E = \frac{\Delta E_o}{\tau\omega} \tag{12}$$

where τ is the adhesion retardation time constant as in Eq. (5). The characteristic frequency, ω_c, expressed in Eq. (11) can be considered as the adhesion frequency that is a critical frequency beyond which adhesion does not take place when inertia controls the dynamics of the bonding phenomenon.

Concentrated copolymer solutions often have a frequency range in which the storage modulus, G′, increases with the square of the frequency [12]. In this case, the viscous term and the inertial terms in Eq. (10) will have the same frequency dependency and the copolymer will behave as a solid. Accordingly, for some instances, a term containing the terminal relaxation time, τ_1, should be added to the copolymer density, ρ, in the denominator of Eq. (11).

For a composite matrix, ΔE_o depends on, among other factors, the filler density [13]. With an increase of the density of the filler particulates in the matrix, more particles will be present at the copolymer surface and as a result less polymer surface will be available for bonding. Consequently, increasing filler density should decrease the bonding energy, ΔE_o, and according to Eq. (11), the adhesion frequency, ω_c.

EXPERIMENTS

The experimental apparatus is shown schematically in Figure 1. The setup consists of a motion control system, a bit assembly and specimen system, a force acquisition system, and an image recording system. The bit assembly is made of a rotary motor and the probe attachments and mounted on a panel driven by the motion control system. The motion control system is constructed of a servo system attached to a microprocessor through a *NuDrive* control box and a virtual instrument *LabView* panel on the computer. The setup allows for a motion sequence of the bit assembly with pre-adjusted speeds and durations.

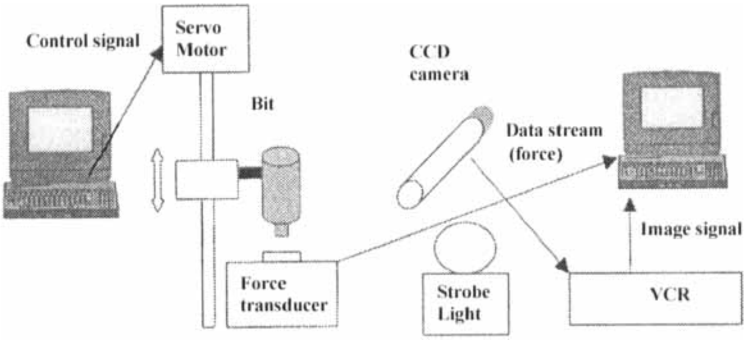


FIGURE 1 Experimental apparatus.

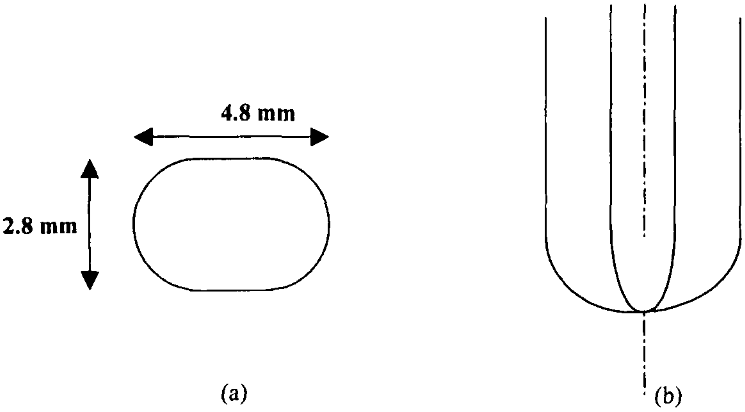


FIGURE 2 Bit geometry: (a) Cross sectional view; (b) Side view.

The geometrical specifications of the bit used in the experiments reported in this paper are depicted in Figure 2. The bit is made of PVC plastic with a rectangular cross-section whose edges are rounded out. The tip of the bit is also rounded out and blended smoothly with the principal non-axisymmetric cross-sectional geometry of the bit. This bit geometry is such that, rotating about its axis, the bit induces an oscillatory motion on the polymer interface. The bit rotation is supplied by a Brasseler Upower drill at high rates in the range of 600 to 35,000 rpm and a small dc motor at low rates from 50 to 600 rpm. The rotational speed of the bit is measured using the flash rate of a strobe light before and after each individual experiment.

In the experiments, the tested polymers are placed inside a cylindrical cavity of a specimen holder made of Plexiglas$^{\mathrm{TM}}$. The cavity has a diameter of 7 mm and a depth of 4 mm. The interaction of the copolymer interface and the rotating bit is characterized by measuring the instantaneous force due to the interaction as the bit approaches the polymer surface. To this end, the specimen holder is mounted on the open end of a sensitive cantilever transducer with EA-06-125PC-350 type strain gages for force measurements. The force transducer has a bending stress of 10 ksi (69 MPa), and a deflection of 0.053 cm/N. The transducer is connected to P3500 strain indicator with an output readable by an A/D board. The data acquisition system in the setup employs a National Instruments board and a microprocessor. A LabView control program passes the force signal through a digital low-pass filter and saves the data onto spreadsheet files for post-processing. A digital video imaging system and a high-resolution B and W CCD camera are also used to capture the polymer-bit dynamic interactions.

Five commercially-available composite materials are used in this study. Their material properties are summarized in Table I. The matrix of all these composites is primarily made of bisphenol A-glycidyl methacrylate (BIS-GMA) and triethylene glycol dimethacrylate (TEGDMA). Their major differences arise from the different filler particle size, filler content and filler materials. Z100 A3.5 and Z100 A4.0 are identical except for the pigment materials; therefore, their physical properties are expected to be close. The Perfection Al and Perfection C1 materials have also similar physicochemical properties. One notices that P50 has the highest concentration of filler particles.

TABLE I Properties of the tested composites

Trade name/manuf.	*Filler particles, weight %, size*
Z100 A3.5-3M	Zirconia and silica, 84.5, 0.6 μm
Z100 A4.0-3M	Zirconia and silica, 84.5, 0.6 μm
P50-3M	Zirconia and silica, 87.5, 0.6 μm
Perfection A1-Denmat	Silanated synthetic silica, 48(+/−0.38) 0.01 ~ 0.04 μm
Perfection C1-Denmat	Silanated synthetic silica, 48(+/−0.38) 0.01 ~ 0.04 μm

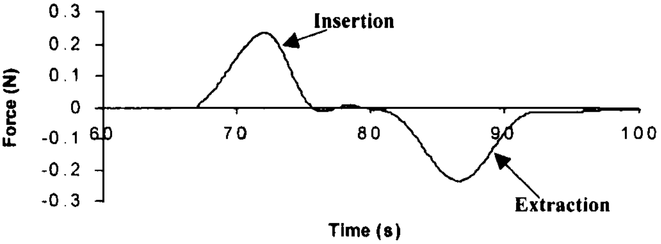
Special care is taken to align the axes of the cylindrical cavity and the bit during the experiments. The composite is syringed into the cavity until the free surface is approximately level with the upper surface of the specimen holder. The composite is then compacted and its surface leveled off using a Teflon-coated stick.

Using the setup, the bit rotating at different speeds plunged into the polymer-filled cylindrical cavity and subsequently withdrew. The bit assembly was programmed to a preset sequence of motions in all cases. The bit was moved vertically downward at an axial velocity of 0.5 mm/s and inserted into the polymer sample up to the point where the tip of the bit was 2 mm below the initial free surface of the polymer. After a 5-s pause, the bit assembly's motion was reversed and the bit extracted from the cavity at the same axial velocity.

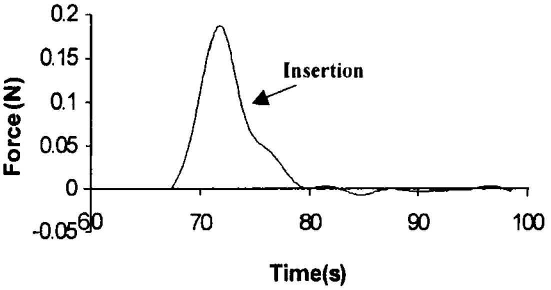
RESULTS

Our experimental results are presented in terms of the instantaneous interfacial force *versus* the position of the bit tip expressed as the lapsed time during the experiment. Figure 3-a is the representative force-distance curve for Z100 A4.0 composite for a non-rotating bit. In this figure, the positive force represents the downward force of the bit onto the polymer surface during the insertion phase. For comparisons, the same force-distance curve for a bit rotating at a high-enough speed such that no tack could be observed is provided in Figure 3-b.

More importantly, the experimental observations and data at different rotational rates confirmed that there existed a minimum frequency above which there was no adhesive bonding between the polymer matrix and the rotating bit. The characteristic force-time curves of the bit rotating at different speeds for different materials indicated that the maximum extraction force became smaller with the bit rotating faster, and disappeared as the rotation speed exceeded 140 rpm for Z100 A4.0 resin and 110 rpm for P50 resin. The areas under the curves in a force-distance plot represent the total energy of interaction during the insertion and extraction phases. A relationship between the extraction energy and the bit rotation speed also indicated



(a) Non-rotating bit.



(b) Bit rotating at 180 rpm.

FIGURE 3 Characteristic force-time curves for Z100 A4.0 composite during an insertion-extraction cycle.

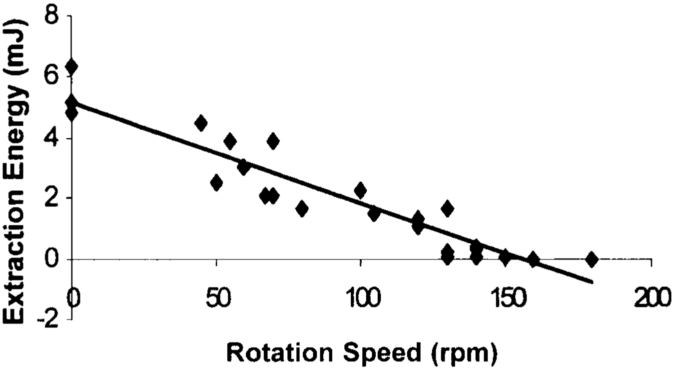


FIGURE 4 Relationship between extraction energy and rotational speed for Z100 A4.0 composite.

that the extraction energy decreases almost linearly with increasing bit rotation up to the critical rotational speed, as is provided for one of the tested copolymers in Figure 4.

TABLE II Critical rotational speeds for the tested composites

Composite	*Critical rotational speed, rpm*
Z100 A3.5	135
Z100 A4.0	140
P50	110
Perfection A1	190

The critical rotational speeds measured for the tested materials are listed in Table II. When the bit was rotating beyond the critical rotational speed, separation between the bit tip and the resin occurred instantaneously during the extraction phase; no resin was detected on the bit and a zero force was recorded on the transducer. By comparison, there was a strong bonding between the bit and the resin for all non-rotating cases. Because of the bit configuration, adhesion frequency for each tested composite is twice the corresponding critical rotational speed in Table II.

DISCUSSION

In our experiments with the non-rotating bit, the approaching bit initially stretches the surface of the polymer matrix in the absence of interfacial wetting. According to Figure 3-a, the resultant interfacial force between the polymer and the bit increases at a slow rate for a fraction of a second beyond the point that the bit has reached the free surface. In this initial interval, the force is due to the elastic deformation of the polymer matrix that progresses at a constant rate. This results in a linear increase of the force with time. A reorientation of the polymeric molecules at the interface has to take place to account for the presence of the penetrating solid surface, upon which a meniscus forms and wetting occurs. Beyond this point, the force on the bit is due to a combination of the increasing wetted interfacial area and the continued deformation of the polymer matrix. The relative importance of these two factors can be estimated from additional experimental observations. As soon as wetting occurs, the rate of increase of the interfacial force with time shifts to a higher value. At the conclusion of the insertion phase, the bit finally is stopped and the viscoelastic response of the polymeric matrix relaxes the force on the bit to zero. In the extraction phase, the force on the bit is represented with a negative sign. The bit is removed from the matrix with the same axial speed used in the previous phase. With the wetted area on the bit surface intact, the extraction force is the mirror image of the insertion force. A comparison of the these two forces when the bit is inside the matrix indicates that the interfacial force is primarily due to the viscoelastic deformation of the matrix, as in the extraction phase the wetted area remains constant.

Rotating at 180 rpm, the measured force *vs.* time curve for the bit is presented in Figure 3-b. For this case, the bit is inducing an interfacial oscillation that is larger than the composite's adhesion frequency. Interestingly, it is exhibiting a force *vs.* time curve similar to the non-rotating bit during the insertion phase. However, the initial stretching of the free surface does not give rise to wetting, but instead the surface breaks up and the bit continues the viscoelastic deformation of the composite matrix as it advances downward into the polymer. A remarkable observation is the fact that the wetting of the non-rotating bit and the surface rupturing of the rotating bit occur at the same penetration depth of the bit and when the bit experiences the same interfacial force. Once the copolymer surface is broken, further penetration of the rotating bit deforms the matrix as it also induces production of additional free surface. The combined effects give rise to a rate of increase of the interaction force that is slightly less than the rate of the non-rotating bit. For the rotating bit, the matrix deformation is not constrained by adhesion to the solid wall and, therefore, the resultant force will be less than the wetted case. This observation reinforces the assertion that the measured force is principally due to viscoelastic deformation of the composite matrix and not the interfacial mechanics.

With the rotating bit standing still, the matrix relaxation around the tip of the bit yields additional positive force on the bit. This force goes to zero as the bit begins its ascent out of the composite adhesive. As the bit continues to ascend, there is no detectable bonding between the matrix and the bit when the bit is rotating faster than the critical speed. Figure 4 shows extraction energies experienced by the bit rotating at and below the critical rotational speed of the polymer matrix. At these frequencies, the bonding–debonding phenomenon at the interface induces similar deformational energies to the matrix. The fact that the extraction energy is decreasing with frequency qualitatively supports the arguments presented in the analysis.

The experimental results verify the existence of adhesion frequency. When the polymer interface is vibrated above the adhesion frequency, no adhesion occurs at the resin/solid interface. Additional information on the actual thermophysical properties are needed to make a direct comparison between our analysis and the critical induced frequencies obtained for the tested materials. However, consistent with our theoretical approach, we can confirm that denser, more viscous resins possess a lower critical frequency compared with lighter, less viscous resins. According to the presented analysis, the energy required to prevent adhesive bonding depends on properties such as density, modulus of elasticity and viscosity. We expect composites with higher values of any of these properties will have lower critical rotation speeds. P50 has higher filler content but similar polymer matrix and identical filler particles in comparison with Z100 composites; it is then expected that P50 will have a higher viscosity and density. As summarized in Table II, P50 has a lower critical rotation speed than Z100 composites. Z100 A3.5 and Z100 A4.0 are essentially identical composites except for the pigments in the materials. Therefore, their critical rotation speeds are expected to be close. Perfection A1 has the lowest viscosity and modulus, therefore, the highest critical rotational speed.

For the case of inertia-dominated matrix deformation, our analysis predicts that the adhesion frequency is larger when the adhesion energy, ΔE_o, is larger. The adhesion energy of a copolymer matrix depends on a number of factors such as concentration, size distribution and geometry of the filler particles in addition to matrix interfacial properties. For copolymers with similar filler size distribution and geometry, an increase in filler concentration reduces the bonding energy. Therefore, according to this equation, a higher filler concentration will reduce the adhesion frequency for a given matrix. The data in Table II agree qualitatively with this assessment while suggesting that the dependency between filler concentration and adhesion frequency can be highly nonlinear, at least in the limit of high filler concentrations.

The observed shift in adhesion frequency can be attributed to changes in the bonding energy as well as inertial and viscoelastic properties of the composite matrix. Which of these factors plays a more dominant role in frequency shift for the tested polymers? Finding an answer to this question requires additional theoretical and experimental work.

CONCLUSIONS

In this paper we have introduced the concept of adhesion frequency. The dynamic adhesion phenomenon between a composite matrix and solid surfaces has been studied through theoretical analysis and experimental tests. It is confirmed that an oscillation at the solid/liquid interface induced by solid probes can effectively prevent an adhesive material from adhering to the probe if the frequency of oscillations is beyond a critical value that we have introduced as adhesion frequency. The adhesion frequency depends on the thermophysical properties of the two media, including the adhesive bonding energy of the interface, the retardation time of the bonding kinetics and the viscoelastic properties of the composite matrix. We have argued that polymers with higher bonding energies, and lower viscosities and densities, have a larger adhesion frequency. Our experiments on five commercially-available copolymers indicate that the polymers with higher solid particle concentrations have lower adhesion frequencies. We have shown that this observation is in qualitative agreement with the analysis we have presented.

For a better understanding of parameters that influence the adhesion frequency additional experimental work needs to be performed. The reported experiments all were conducted using the same operational parameters. One can study the adhesion frequency while varying the axial speed of the bit, the geometry of the bit and the cavity housing the tested polymers, as well as the bit surface material. Material characterization of the polymers used in the experiments will assist in a more direct comparison between the analysis and the experimental data.

References

[1] Borgly, M., Grohens, Y., Labbe, C. and Schultz, J., *Int. J. Adhesion Adhesives* **17**, 257 (1997).

[2] Abedian, B., Racz, L. M., O'Leary, J. P. and Millstein, P. L., *Method of Shaping an Adhesive Material* (U.S. Patent Application, 1998).

[3] Andrews, E. H. and King, N. E., *Surface Energetics and Adhesion*, In: *Polymer Surfaces*, Clark, D. T. and Feast, J. F. Eds. (John Wiley, New York, 1978), Chap. 3, pp. 47–63.

[4] Gent, N. and Kinloch, A. J., *J. Polymer Sci.* **A2-9**, 659 (1971).

[5] Wetzel, F. H., *ASTM Bull.* **221**, 64 (1957).

[6] Andrews, E. H. and Kinloch, A. J., *Proc. Roy. Soc. Lond.* **A332**, 385 (1973).

[7] Wu, S., *Polymer Interfaces and Adhesion* (Marcel Dekker, Inc., New York, 1982).

[8] Cherry, B. W. and Muddaris, S. E., *J. Adhesion* **2**, 42 (1969).

[9] Rutzler, J. E. and Savage, R. L. Eds., *Adhesion and Adhesives: Fundamentals and Practice* (John Wiley and Sons, New York, 1954), pp. 130–138.

[10] Bates, R., *J. Appl. Polymer Sci.* **20**, 2941 (1976).

[11] Ferry, J. D., *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York, 1980).

[12] Charrier, J. M., *Polymeric Materials and Processing* (Hanser Publishers, New York, 1991).

[13] Gent, A., Hamed, G. R. and Hung, W. J., "Adhesion of elastomers: Dwell time effects and adhesion to fillers" (*Proc. 23rd Ann. Meeting of Adhesion Soc.*, Anderson, Gregory, Ed., Myrtle Beach, SC, 2000), pp. 6–9.