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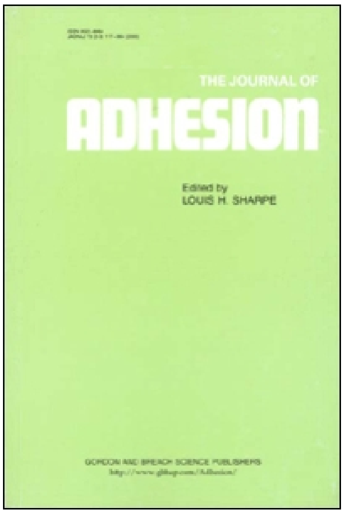

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Surface Tension of Molten Glass from Drop Profile. Application to the Characterization of the Interface in Glass/Polymer Blends*

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A modified drop shape method has been developed to allow the simple determination of the surface free energy of a mineral glass. Our approach is based on the study of the profile of a large sessile drop of glass. The drop is formed by heating a glass cylinder settled on a horizontal solid plane.

The experimental parameters, in particular the size of the glass drop, leading to the accurate characterization of the surface free energy, have been determined by using mercury as a model of a high surface free energy liquid. It has been shown that the ratio between the diameter of the drop and the capillary length, $(\gamma/\rho\mu)^{1/2}$, must be of the order of 10.

In this paper, practical details and results of measurements are presented for a series of four different glasses. A clear relationship between glass composition and surface free energy is observed. In particular, tin oxide reduces significantly the surface free energy of zinc phosphate glass. The coalescence of glass particles is probably related to glass surface and glass/polymer interfacial free energies. A discussion on how this may impact glass/polymer blend processability is presented.

KEY WORDS Surface tension; interfacial tension; phosphate glass; large drop profile; glass/polymer blends; surface free energy; sessile drop; contact angle; composite.

I INTRODUCTION

In recent years, researchers at Corning have searched for durable phosphate glasses capable of compounding with high temperature polymers to yield dimensionally-stable, stiff, injection-moldable materials for high temperature application (Cortem™ glass/polymer blends). By far the best glasses discovered to date, in terms of glass stability, chemical durability and low working temperature, are mixed-alkali, zinc-pyrophosphate compositions.[1] Such glasses are melt mixed with various high temperature thermoplastics in a heated twin-screw extruder to produce, under high shear, a fine-grained dispersion of glass droplets (1 to 100 μm) in a polymer matrix.

As in any composite material, the characteristics of the interfacial region between the phosphate glass particles and the polymer govern numerous features of the system such

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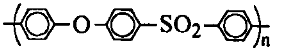
as the rheology in compounding and molding, the microstrucure and the mechanical properties of the blend.

Although several techniques, either microscopic or spectroscopic, exist to study interfaces or interphases between the organic and mineral phases,[2] it is not an easy task in a blend or a microcomposite.

In this work, a thermodynamic approach to the glass/polymer interface characterization is used. It is based on surface tension measurements and interfacial tension calculation as a function of glass composition. These thermodynamic parameters allow one to understand better the properties of different glass/polymer combinations. Therefore, a simple method to measure the surface tension of phosphate glasses near the compounding and transformation temperature of glass/polymer systems is proposed. The calculation of the glass/polymer interface tension is then illustrated with a practical example using polyethersulfone,  , as the high temperature polymer matrix. In comparison with experimental methods allowing one possibly, to measure the glass/polymer interfacial tension such as the "imbedded fiber retraction",[3] one advantage of our thermodynamic approach is simplicity.

The mineral glasses considered belong to a new family of durable phosphate glasses having a glass transition temperature between 275 and 375°C. They have melt viscosities, η, of 10^7 to 10^5 Poises at the compounding temperature of 380 to 430°C. Such high viscosity values do not permit the simple measuring of surface tension with classical tensiometric techniques consisting of dipping a ring, a plate or a cylinder in the liquid, so that a drop shape method which allows easy measurements at high temperature and viscosity has been used.

II THEORETICAL

II.1 Surface Tension of Molten Glass

The method is based on the examination of the profile of a liquid glass drop. The dimensions of a sessile drop have been used for at least a century to derive the surface tension of a liquid. The usual method is based on the classical equation of Bashforth and Adams[4] which defines the shape of a meniscus in a general situation.

In the case of a very large drop, the profile of the drop takes the shape of a thick "pancake". The profile is defined by the balance of the horizontal forces acting in the cross-section of the drop. The equilibrium between hydrostatic (P) and surface tension forces (Figure 1) leads to the equation[5]

$$\int_0^e z\rho\mu\,dz = \gamma_{sg} + \gamma_g - \gamma_s \tag{1}$$

where ρ is liquid density, μ gravitational acceleration, and γ is the interfacial tension at the solid/glass (sg), glass/air (g), and solid/air(s) interfaces. Integration of equation (1), combination with Young's equation

$$\gamma_s = \gamma_{sg} + \gamma_g \cos\theta \tag{2}$$

where θ stands for the contact angle, and application of the double angle relation for $\cos\theta$ leads to:

$$\gamma_g = \frac{e^2 \rho \mu}{4 \sin^2(\theta/2)} \tag{3}$$

If we consider now the distance, h, between the top of the drop (apex) and the equator (Figure 1), it is equal to e when $\theta = \pi/2$, so that the next equation can be also deduced:

$$\gamma_g = \frac{h^2 \rho \mu}{2} \tag{4}$$

This is also the definition of the capillary constant, $a^2 = 2\,\gamma/\Delta\rho\mu$, which was derived earlier by Burdon.[6]

The validity of the relationships (3) and (4) is dependent on the size of the liquid drop, but for a drop sufficiently large it must be verified that

$$e = \sqrt{2}\, h \sin(\theta/2) \tag{5}$$

when $\theta > \pi/2$. Furthermore, the shape of the drop resulting from the balance of gravitational and surface forces, the appropriate dimension of the drop can be compared to the capillary length, k^{-1}, which is given by:

$$k^{-1} = \left(\frac{\gamma}{\rho\mu}\right)^{1/2} \tag{6}$$

Mercury was used as a model high-surface-tension liquid to determine the minimum drop size required for an accurate determination of γ_g from equations (3) and (4).

II.2 Glass/Polymer Interfacial Tension

Measuring the glass/polymer interfacial tension, γ_{gp}, at the compounding temperature of glass/polymer blends ($T \approx 400°C$) is not easy from practical point of view. Nevertheless, an indirect measurement can be easily derived from the Young's equation, in considering that

$$\gamma_{gp} = \gamma_g - \gamma_p \cos\alpha \tag{7}$$

where γ_p is the polymer surface tension and α the Young contact angle at the triple line liquid polymer/glass/air and γ_g is the glass surface energy in air. The use of equation (7) requires measurements of α on a smooth and flat glass surface, therefore measurement must be made below the deformation temperature of glass. The main objective of this study is to evaluate the variation of γ_{gp}, $\Delta\gamma_{gp}$, as a function of glass composition given by

$$\Delta\gamma_{gp} = \Delta\gamma_g - \gamma_p \,\Delta\cos\alpha \tag{8}$$

for a given polymer matrix.

As mentioned in the experimental section, α varies little for the polymer and glass compositions considered so that equation (8) may be simplified to:

$$\Delta\gamma_{gp} \approx \Delta\gamma_g \tag{9}$$

This simple relationship means that Antonoff's rule[7] ($\gamma_{12} = \gamma_1 - \gamma_2, \gamma_1 > \gamma_2$) may be valid at the phosphate glass/polymer interfaces, at least for the polymer and glass compositions of this study.

A comparable situation is observed at water/hydrocarbon interfaces where water hydrogen bonds do not play any role at the interface. For such systems, Antonoff's rule permits also an acceptable prediction of γ_{12}. In this study, unexchanged interactions across the glass/polymer interfaces are probably those of an ionic nature.

III EXPERIMENTAL

The glass compositions used to prepare glass/polymer blends belong to the $P_2O_5 - ZnO - R_2O$ system, where R is a group IA mixed-alkali system. The preferred composition range is, in mol%:[1] P_2O_5 30-36, ZnO 30–49, R_2O 12–25, Al_2O_3 1–3.5 and SiO_2 0–2. Three examples (A, B and C) of such glasses have been considered with a fourth example (D) for which 5 mole % of SnO has been introduced in the glass composition. After melting at ≈ 1000°C, patties were poured in 10 × 20 cm molds and allowed to cool in air until rigid enough to be placed into an annealer. These 1.5 cm thick glass slabs were then annealed overnight near 300°C.

To establish the validity conditions of equations (3) and (4), the minimum size of liquid drops was estimated by measuring at 20°C the surface tension of pure mercury (Hg = 99.9999 %, Rhône Alpes Mercury, France) with the proposed method. As demonstrated by Bonfield,[8] drop size and solid substrate impact the surface tension measurement of mercury. In this study, a series of mercury drops having volumes of 0.5 to 1.25 cm^3 were deposited on a smooth and horizontal plate of Teflon PTFE. For each drop, the parameters *h*, *e*, θ and diameter, *d*, (Figure 1) were measured with a Ramé-Hart Contact Angle Goniometer. The mean values of *h*, *e* and θ are reported in Table I. The measured surface tension of mercury using sessile drop or maximum pressure bubble (CO_2) methods is 486.5 ± 2 $mN.m^{-1}$ at 20°C.[9] Equations (3) and (4) converge to within 1% of this value when the ratio d/k^{-1} is of the order or greater than 10 (Table I). For mercury, k^{-1} is equal to 1.91×10^{-3} m at 20°C.

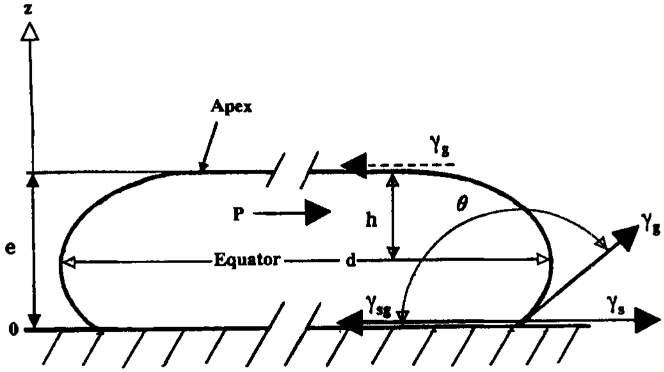


FIGURE 1 Forces acting in a large drop and parameters defining the profile of a thick "pancake" ($d \approx 5 \times e$).

TABLE I

Profile parameters of heavy droplets of mercury on Teflon, surface tension calculated with Eq. [3], γ_1 and Eq. [4], γ_2 and mean value of $\bar{\gamma}$. In the ratio d/k^{-1}, d is the drop diameter and k^{-1} the capillary length ($k^{-1} = 1.91$ mm for mercury at 20° C).

Drop Volume (cm^3)	h (mm)	e (mm)	d (mm)	θ (deg)	γ_1 (mN.m^{-1})	γ_2 (mN.m^{-1})	$\bar{\gamma}$ ($\pm$5mN.m^{-1})	d/k^{-1}
0.50	2.74	3.66	15.28	145.5	500.8	489.9	495.4	8.0
0.75	2.72	3.65	18.72	146.8	493.5	484.0	488.8	9.8
1.00	2.70	3.64	21.77	147.0	486.3	480.7	483.5	11.4
1.25	2.70	3.64	24.45	147.0	486.3	480.7	483.5	12.8

From preliminary experiments, it has been found that the condition $d/k^{-1} \approx 10$ is satisfied with liquid phosphate glass when drops of a volume of about 2.5 cm^3 are formed on stainless steel.

Glass drops were formed from glass cylinders (diameter ≈ height ≈ 1.5 cm) positioned vertically on horizontal stainless steel plates (NS30) inside the environmental chamber of the contact angle goniometer (Figure 2). Starting from a vertical cylinder assists the formation of a perfectly axisymmetric drop. The power of the electric heating system of the chamber was boosted in order to be able to heat up 500°C. Electronic regulation ensures a temperature control at ± 1°C.

Most of the measurements were conducted at 440°C, near the average glass/polymer compounding temperature. The densities of glasses, ρ, at this temperature were evaluated from densities measured at 20°C and from their coefficient of thermal expansion, of the order of $15 \times 10^{-6}\,K^{-1}$,[10] leading to a very small variation of density, $\Delta\rho/\rho$, of $-45 \times 10^{-6}\,K^{-1}$ (with $\Delta T = 420$ K, $\Delta\rho/\rho < 2$ %).

To illustrate the calculation method of glass/polymer interfacial tension, polyethersulfone (Victrex PES 3600G, ICI, USA) was chosen as representative of a high-temperature, engineering thermoplastic. Its contact angle, α, on A, B, C and D phosphate glasses was measured at 350° C under nitrogen, to avoid polymer oxidation. The polymer drops were formed by using individual cylindrical pellets set vertically on smooth glass disks. The constant value of α at the equilibrium was obtained after 0.5 hour of contact due to the high viscosity of PES at 350°C ($\eta \approx 4 \times 10^3$ Poises).

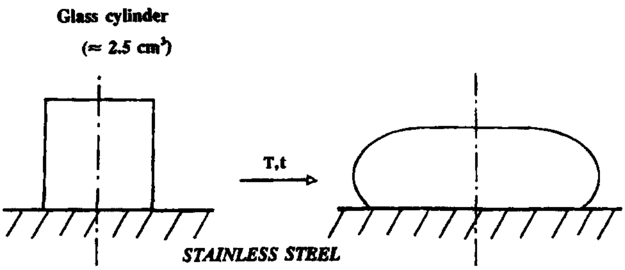


FIGURE 2 Formation of large drop of glass.

IV RESULTS

Preliminary experiments[11] carried out with a phosphate glass at 500°C showed us the the surface tension obtained with equations (3) and (4) is not very dependent on the spreading time, $t(0.5 < t < 2\,\text{hrs})$, of the molten glass drop on stainless steel, so that the measurements of h, e and θ parameters can be effected without waiting for complete wetting equilibrium of the liquid glass on the solid substrate. This observation may be explained by the very low speed of spreading, of the order of 10^{-6} m/s, of the molten glass on stainless steel leading to a sequence of quasi-equilibrium situations.

Figure 3 presents another example concerning C-glass and showing that the measured surface tension stays relatively constant *versus* spreading time of the glass drop at 440°C. However, the relationships (3) and (4) are valid only when the ratio d/k^{-1} is at least of the order of $10\,(k^{-1} \approx 3 \times 10^{-3}\,\text{m})$. At 440° C, forming the heavy drop of glass from the glass cylinder requires about 2.5 hours given the high viscosity of glass at this temperature ($\eta \approx 2.5 \times 10^5$ Poises).

The surface tension values, γ_g, resulting from several experiments are reported in Table II. It can be noticed that the results obtained from equations (3) and (4) are very close. The error on the mean surface tension values, $\bar{\gamma}_g$, is of the order of 2% ($\bar{\gamma}_g$ is the average of at least 4 measurements).

In order to evaluate the phosphate glass/polyethersulfone (PES) interfacial tension near the compounding temperature, the contact angle of PES, α, at 350°C was measured on A, B, C and D glasses. Whatever the glass composition, α at equilibrium (reached after 0.5 hours) was found equal to 40 ± 2 degrees, demonstrating that glass/polymer interactions are not very dependent on glass composition for this glass family and polyethersulfone.

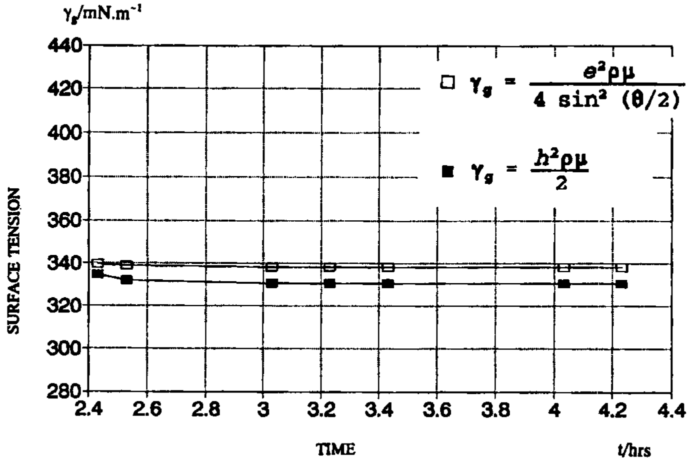


FIGURE 3 Surface tension of C-glass *versus* time at 440°C.

TABLE II
Surface tension in mN.m^{-1} of zinc phosphate glasses at 440°C. $\bar{\gamma}_g$ is the average value.

Glass	γ_g from Eq. [3]	γ_g from Eq. [4]	$\bar{\gamma}_g$
A	305.5	305.9	306 ± 2
	308.4	305.9	
	302.3	307.3	
B	291.7	290.9	287 ± 7
	277.2	288.3	
C	333.3	331.6	326 ± 7
	331.5	324.8	
	320.4	316.7	
D	194.3	192.5	195 ± 5
(contains tin oxide)	190.3	201.0	

V DISCUSSION

The phosphate glasses considered have a surface tension between 200 and 330 mN.m^{-1} at 440° C, depending on their composition. D-glass has the lowest surface tension and, since it is the only glass containing tin oxide, it can be concluded that 5 mole % of tin oxide reduces by about 100 mN.m^{-1} ($\approx 30\%$) the surface tension of zinc phosphate glass. This is consistent with Rubestein's findings[12] for the effect of tin oxide on the surface tension of soda-lime silicate glass.

The glass surface tension, γ_g, determines the glass/polymer interfacial tension, γ_{gp}, as written with equation (7). In the case of polyethersulfone, the glass/polymer interactions do not apparently vary from one glass to another, the polymer contact angle on glasses at 350°C staying around 40 degrees whatever the glass composition. Therefore, it can be concluded that a decrease of 100 mN.m^{-1} for γ_g induces an equivalent reduction of the glass/polymer interfacial tension, γ_{gp} ($\Delta\gamma_{gp} \approx \Delta\gamma_g$, see equation (9)). Of course, we admit implicitly that the glass/polymer interactions are not drastically modified when temperature is increased from 350 to 440°C and that what is observed at 350°C is transposable to 440°C. This implies that $\partial\gamma_{gp}/\partial T$ is also not very dependent on glass composition. Moreover, measurements of the contact angle at 300°C lead to the same conclusion.

This result ($\Delta\gamma_{gp} \approx \Delta\gamma_g$) is consistent with the notion that tin oxide strongly modifies the ionic interactions in phosphate glasses but has a small effect on Van der Waals (and eventually acid/base) interactions between glass and polymer across the interface.

The decrease of γ_{gp} produced by tin oxide is also in good agreement with observations made during compounding and molding experiments of glass/polymer blends. It has been noticed that the coalescence tendency of glass particles is greatly reduced at high temperature (and relatively low viscosity) when the phosphate glass contains tin oxide. This is consistent with the coalescence tendency of glass being controlled by the glass/polymer interfacial tension and, therefore, the glass surface tension, since $\Delta\gamma_{gp} \approx \Delta\gamma_g$.

VI CONCLUSION

The measurement of the surface tension of zinc phosphate glass near the compounding and molding temperature of glass/polymer blends is possible using drop profile analysis of large glass droplets shaped from glass cylinders. In comparison with other experimental methods used to measure γ_g (Bashforth and Adams analysis,[13–14] fiber elongation,[15]) the modified shape analysis technique used in this study is very simple and gives reliable values with a reasonable precision, provided that the drop size satisfies the condition $d/k^{-1} \geqslant 10$. Although this work has been limited to low-temperature-melting glass, it can be generalized to other glasses or materials whose high viscosity complicates the use of classical tensiometric methods.

It has been also demonstrated that the glass composition determines the surface tension of glass and, therefore, the glass/polymer interfacial tension and the stability of glass/polymer blends. The addition of 5 mol% tin oxide to the glass strongly reduces the surface and interfacial tensions.

The glass/polymer interfacial has not been precisely measured but the variation of this parameter with glass composition has, nevertheless, been established.

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