

Glass and polymer: wetting and adhesion

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The use of glass–polymer compounds is on the advance as for the finishing of glass products and for the development of materials to be used in new applications. The results from wetting and adhesion experiments of thermoplastic polymers on glass surfaces without coupling agents are discussed. The attempt to use the thermodynamic work of adhesion as a measure of adhesion proved to be unsuccessful, as it is difficult to characterize glass according to surface energy. Contact angle measurements of melted polymers on glass surfaces show that the type of silicate glass applied does not influence the contact angle. The wetting is controlled by the viscosity of the polymer melt, and the kinetics follows a power law. The fact that non-polar polymers show a low level of adhesion on glass surfaces is based upon results of strength measurements of compounds between glass and polymers. Apart from polarity, mechanical and thermal properties of polymers play a decisive role. Great importance is attributed to the ability to relieve stress, since the observed cohesion failure inside the glass is caused by brittle polymers. Adhesion, however, is insignificantly dependent on glass composition. If the joint is not achieved by polymer melting but by a solution of the polymer, the surface property (acid-base affinity) of the glass becomes a critical factor, and adhesion may fail completely.

Glas–Polymer-Verbunde: Benetzung und Haftung

Glas–Polymer-Verbunde erlangen wachsende Bedeutung bei der Veredelung von Glaserzeugnissen und bei der Entwicklung von Werkstoffen für neue Anwendungen. Es werden die Benetzung und die Haftung von thermoplastischen Polymeren auf Glasoberflächen ohne haftvermittelnde Schichten bestimmt. Der Ansatz der thermodynamischen Adhäsionsarbeit als Maß für die Haftung führt nicht zum Ziel, da die oberflächenenergetische Charakterisierung der Gläser schwierig ist. Bei Randwinkelmessungen aufgeschmolzener Polymere auf Glassubstraten ergibt sich, daß sich der Benetzungswinkel unabhängig von der Zusammensetzung des verwendeten Silicatglases bildet. Die Benetzung wird bestimmt durch die Viskosität der Polymerschmelze und folgt einem Potenzgesetz. Bei Verbundfestigkeitsmessungen zwischen Gläsern und thermoplastischen Polymeren ergibt sich, daß unpolare Polymere nur geringe Haftung an Glasoberflächen zeigen. Neben der Polarität spielen auch mechanische und thermische Eigenschaften der Polymere eine entscheidende Rolle. Dabei kommt der Fähigkeit zum Spannungsabbau durch Dehnung eine große Bedeutung zu, da bei spröden Polymeren Kohäsivbrüche im Glas beobachtet werden. Die Haftung ist hingegen wenig von der Zusammensetzung des Glases abhängig. Wird die Verbindung nicht durch Aufschmelzen des Polymers erzielt, sondern eine Polymerlösung aufgebracht, so wird die Oberflächeneigenschaft (Säure-Base-Affinität) des Glases entscheidend, und es kann zum vollständigen Haftungsversagen kommen.

1. Introduction

The number of application areas for glass–polymer compounds has increased. Today these compounds are already widely in use for reinforced plastics, for laminated safety glass and for direct glazing in car manufacture, for applications in the building and construction industry (insulating glass, “Structural Glazing”), and in the optical industry. Apart from that there has been an increase in importance as for polymer protective coatings on sheet glass and on container glass. Furthermore, the combination of two very different materials opens up an enormous potential for developing new products and for the processing of current goods.

Adhesion promoters often improve the adhesion properties of plastics. In these cases coupling is at least partly achieved by chemical bonds [1]. Further examinations deal with the corrosive effect of water on glass–polymer adhesive bonds [2]. It is, however, of major interest which factors determine the wetting and adhesion of thermoplastic polymers on glass and which role can be attributed to the specific type of glass.

In some application cases the additional use of coupling agents is not intended or is impossible. Because of that, and with the intention of achieving a better understanding of the mechanisms, some examinations will be presented, that treat the wetting and adhesion between thermoplastic polymers and different types of glass.

Various theories on interfacial mechanisms have been put forward. The adsorption theory, by which processes of adhesion can be described, is most widely accepted and its formulation is most advanced [3]. This theory is based on the assumption that specific energy

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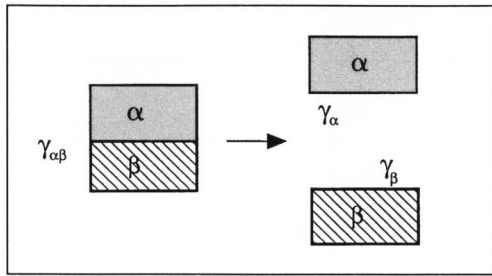


Figure 1. Separation of an adhesive joint consisting of phases α and β .

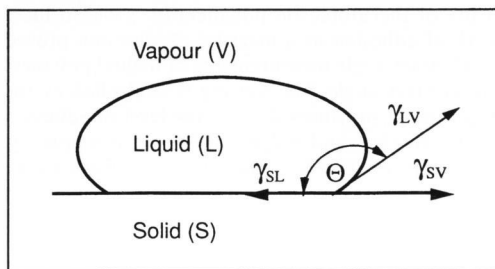


Figure 2. Sessile drop.

states can be attributed to surfaces and interfaces, i.e. the surface energy γ_α of phase α and the interface energy $\gamma_{\alpha\beta}$ on the interphase between phases α and β (figure 1). In order to separate a compound by creating two new surfaces, the thermodynamic work of adhesion W^{Ad} is required. It can be described as follows:

$$W^{Ad} = \gamma_\alpha + \gamma_\beta - \gamma_{\alpha\beta} . \quad (1)$$

According to this approach the work of adhesion as a measure of compound strength is determined by the surface and interface energies, unless chemical bonds are formed on the interface. In theory the adhesive behaviour can be predicted with the aid of these material properties on condition that energy-dissipating fracture side effects are neglected.

Since it is often impossible to measure interface energies, the adhesion of a drop on a solid phase is used instead. A correlation between the required qualities can be derived from the energy equilibrium of a sessile drop (figure 2, equation (2)).

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \Theta \quad (2)$$

where the indices V, L, and S stand for vapour, liquid, and solid, respectively.

A combination of equations (1 and 2) results in W^{Ad} by measuring the wetting angle Θ and the surface tension of the liquid (neglecting the spreading pressure):

$$W^{Ad} = \gamma_{LV} (1 + \cos \Theta) . \quad (3)$$

In the following, thermoplastic polymers will be melted on flat glass surfaces in order to make an attempt to infer the thermodynamic work of adhesion from the wetting behaviour. The tested material combination will be critically analyzed as to whether the determined work of adhesion is connected with joint strength. In addition to that a few parameters that determine the wetting and adhesion of thermoplastic polymers on glass will be named.

The great influence of polar groups on adhesion between polymers led to a further development of the theories on wetting and adhesion. According to Fowkes [4 and 5] interfacial interaction can be divided into several partial amounts of energy, i.e. into a "non-polar" term resulting from dispersion interactions $W^{Ad,d}$, and a term being composed of all the other (polar) partial amounts of energy ($W^{Ad,p}$), which is summarized by the following correlation:

$$W_{ij}^{Ad} = W_{ij}^{Ad,d} + W_{ij}^{Ad,p} . \quad (4)$$

Recently a crucial role for achieving adhesion between glass and polymers has been ascribed to specific interfacial interactions between electron-accepting (proton-donating) and electron-donating (proton-accepting) components of compound partners [6]. These are referred to as acid-base interactions, during which charge carriers are, however, not completely transferred. This type is exemplified by the hydrogen bond. Thus, the surfaces with an increased affinity for protons are called basic and those with an increased affinity for electrons are called acidic. That is why pure SiO_2 glass is referred to as acidic, whereas soda lime silicate glass as basic [7]. It is even being considered that the effect achieved by adhesion promoters may be a result of these acid-base interactions [8 and 9]. According to this model, the total work of adhesion is composed of Lifshitz-Van der Waals forces (index "LW", dipole interactions included) and the contribution by acid-base interactions (index "AB") [10]:

$$W_{ij}^{Ad} = W_{ij}^{Ad,LW} + W_{ij}^{Ad,AB} . \quad (5)$$

The determination of this energy part amount of the adhesion energy is problematic because of missing exact surface energy data of the compound participant glass. Later on this problem will be discussed in detail.

The aforementioned approaches can however be applied for a characterization of thermoplastic polymers with regard to surface energy, polarity and acid base affinity. Therefore, wetting tests are made with test fluids on smooth substrate surfaces. Different evaluation methods are applied.

In order to determine the actual compound strength data, it is necessary to split the glass-polymer compounds. Following earlier tests [11 to 13] and the stand-

Table 1. Compositions of technical glasses in wt% (in parentheses in mol%) as given by the producers

	lead silicate glass	borosilicate glass	TV glass (screen)	float glass (white)	E-glass	aluminosilicate glass	basalt glass
SiO ₂	35.0 (64.4)	80.0 (82.7)	63.0 (71.0)	71.7 (70.6)	53.8 (56.9)	60.0 (67.0)	45.96 (50.93)
B ₂ O ₃	—	13.0 (11.6)	—	—	7.0 (6.4)	4.5 (4.3)	—
Al ₂ O ₃	—	2.5 (1.5)	3.0 (2.0)	0.5 (0.3)	13.7 (8.6)	14.5 (9.5)	13.58 (8.84)
MgO	—	—	2.0 (3.4)	3.9 (5.7)	0.4 (0.6)	2.0 (3.3)	9.87 (16.29)
CaO	—	—	2.0 (2.4)	9.5 (10.0)	23.9 (27.0)	10.0 (11.9)	10.25 (12.15)
BaO	—	—	13.0 (5.7)	—	—	9.0 (3.9)	—
K ₂ O	5.0 (5.9)	1.0 (0.7)	8.0 (5.7)	0.2 (0.1)	0.3 (0.2)	—	1.45 (1.02)
PbO	60.0 (29.7)	—	—	—	—	—	—
Na ₂ O	—	3.5 (3.5)	9.0 (9.8)	13.7 (13.1)	0.3 (0.3)	—	2.49 (2.67)
Fe ₂ O ₃	—	—	—	0.1 (0.04)	0.17 (0.06)	—	12.52 (5.21)
P ₂ O ₅	—	—	—	—	—	—	0.45 (0.21)
MnO	—	—	—	—	—	—	0.17 (0.16)
TiO ₂	—	—	—	0.05 (0.04)	—	—	2.71 (2.25)
SO ₃	—	—	—	0.2 (0.15)	—	—	0.30 (0.25)

ard ASTM D 1344 tensile tests based on the “Cross-Lap-Method” [14] were selected from a whole range of available test methods. Most other test methods are based upon specific material properties. That is why these tests such as e.g. the “peel test” are only applicable to certain polymers.

2. Experimental

2.1 Test material

On the one hand, thermoplastic synthetic materials of major technical importance will be used in the following tests. Great attention has been paid to cover a wide spectrum of properties. On the other hand, non-standard polymers, which are already applied to glass-polymer composites, will be used on a par with standard polymers.

The compositions of the various glass types to be tested are listed in table 1. Apart from this wide spectrum of commercial glass types, specimens of soda lime

Table 2. Compositions of investigated glasses in wt% (in parentheses in mol%)

	glass 55	glass 65	glass 80	SiO ₂ glass
SiO ₂	55.0 (55.56)	65.0 (65.42)	80.0 (80.30)	>99.99 (>99.99)
Na ₂ O	27.0 (26.42)	23.5 (22.91)	10.5 (10.21)	—
CaO	15.0 (16.23)	10.0 (10.78)	8.0 (8.60)	—
Al ₂ O ₃	3.0 (1.79)	1.5 (0.89)	1.5 (0.89)	—

silicate glasses are prepared in a platinum crucible. The SiO₂ content is varied from 55 to 80 wt%, which is meant to achieve different levels of basicity for the glass (table 2).

Table 3. Dispersion force components, γ^d , and polar force component, γ^p , of the surface energy, γ , of liquids used for contact angle measurements in mJ/m^2

liquid	γ	γ^d	γ^p
water	72.8	21.8	51.0
glycerol	64	34	30
ethylenglycol	48.0	29	19.0
formamide	58	39	19
dimethylsulphoxide DMSO	44	36	8
tricresylphosphate TCP	40.9	39.2	1.7

Table 4. Surface energy components, γ , γ^{LW} , γ^{AB} , of liquids used for contact angle measurements for the characterization of acidic and basic behaviour, γ^{\oplus} , γ^{\ominus}

liquid	γ	γ^{LW}	γ^{AB}	γ^{\oplus}	γ^{\ominus}
water	72.8	21.8	51.0	25.5	25.5
glycerol	64	34	30	3.92	57.4
ethylenglycol	48.0	29	19.0	1.92	47.0
formamide	58	39	19	2.28	39.6
dimethylsulphoxide	44	36	8	0.5	32
diiodomethane DJM	50.8	50.8	≈ 0		

2.2 Characterization of the surface energy of the test materials

2.2.1 Surface energy, polarity and acid-base characterization of the polymers

In order to characterize the surface energy state of the polymers at room temperature, different evaluation methods are applied that are based upon measuring the wetting properties of test liquids. Here, the theories on wetting and adhesion, which are based on the principles "calculation of interfacial interactions" and "energy additivity" are applied in order to determine both the absolute value of the surface energy and the polarity. Besides a new approach is followed according to which wetting angles are partly a result of specific acid-base interactions.

Droplets of test liquids are placed upon smooth polymer substrates. With the aid of a video camera the wetting angle is observed from the side. The wetting liquids have been entered in tables 3 and 4. By analogy with equation (6) ("geometric mean equation") the required quantities can be determined by the known surface energy parameters γ_{LV}^d and γ_{LV}^p (dispersive and polar surface partial amounts of energy of the test liquid) to be found in table 3, and additionally by combining two wetting tests each [15 to 17]. This determination results in γ_{SV}^d and γ_{SV}^p , i.e. the dispersive and polar surface energy amounts of the solid polymer.

$$1 + \cos \theta = \frac{2\sqrt{\gamma_{\text{SV}}^d \gamma_{\text{LV}}^d}}{\gamma_{\text{LV}}} + \frac{2\sqrt{\gamma_{\text{SV}}^p \gamma_{\text{LV}}^p}}{\gamma_{\text{LV}}} \quad (6)$$

The total surface energy of the polymer is the sum of the partial amounts γ_{SV}^d and γ_{SV}^p .

In order to attain additional information on acid-base properties, an evaluation method was presented that is based on equation (5) [10 and 18]. According to this method the surface energy consists of a partial amount ("LW") due to Van der Waals forces and another one resulting from acid-base interactions ("AB"):

$$\gamma_i = \gamma_i^{\text{LW}} + \gamma_i^{\text{AB}} \quad (7)$$

The acid-base component of the surface energy can be determined according to equation (8) by the acid parameter γ_i^{\oplus} and the base parameter γ_i^{\ominus} . These quantities are known for several test liquids (compare table 4).

$$\gamma_i^{\text{AB}} = 2\sqrt{\gamma_i^{\oplus} \cdot \gamma_i^{\ominus}} \quad (8)$$

These parameters can be ascertained by combining three wetting tests and by formulating equation (9), respectively. On the whole, the required quantities γ_i^{LW} , γ_i^{\oplus} , γ_i^{\ominus} can be derived for any polymer from an equation system made up of three equations.

$$\gamma_{\text{L}_1}(1 + \cos \theta_1) = 2(\sqrt{\gamma_{\text{S}}^{\text{LW}}} \sqrt{\gamma_{\text{L}_1}^{\text{LW}}} + \sqrt{\gamma_{\text{S}}^{\oplus}} \sqrt{\gamma_{\text{L}_1}^{\oplus}} + \sqrt{\gamma_{\text{S}}^{\ominus}} \sqrt{\gamma_{\text{L}_1}^{\ominus}}) \quad (9)$$

Thus, a good description of the surface properties of the polymers is provided by the wetting behaviour of different test liquids.

2.2.2 Surface energy of glasses

First of all the surface tensions of glass melts at high temperatures are measured and calculated in order to characterize the surface energy state of the applied test glasses. In order to do so, a platinum cylinder is placed with its flat side on the glass melt and then pulled up. The maximal weight of the glass meniscus is measured with the help of a precision balance. Using the maximal weight the surface energy of the liquid can be calculated [19]. In order to obtain comparative values of solid glasses at room temperature, the effective surface energy is determined by the Vickers hardness test. This quantity expresses the energy amount that is necessary for the formation of a new surface. For that purpose a Vickers diamond is used not only to make indentations but also to produce radial cracks. The stress intensity factors and the effective surface energies can be evaluated according to the Marshall and Evans method [20]. For comparison the results of both methods are juxtaposed with results of other methods taken from literature.

2.3 Wetting behaviour of thermoplastic polymers on glass surfaces

Cylindrical test specimens of viscous thermoplastic polymers are melted on polished glass surfaces in inert gas (N_2). A modified heat microscope is used as a device

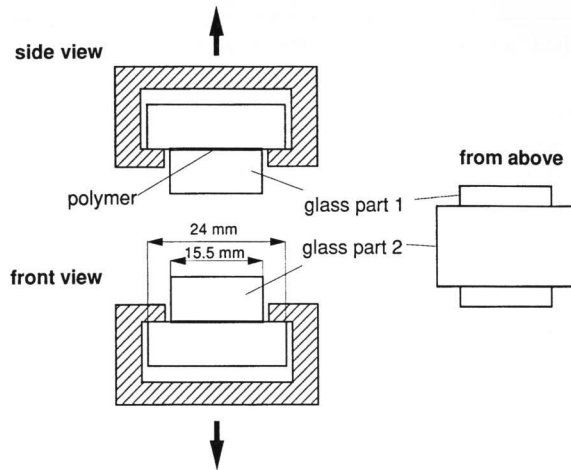


Figure 3. Schematic of the modified "cross-lap" specimen.

for observing the changing shape of a drop. Thus, the advancing wetting angle can be measured (sessile drop method).

Special interest lies in the consideration of the kinetics of the wetting process. In order to ascertain the potential influence of the viscosity of the wetting liquids, the temperature dependence of the viscosity of the polymer melts are measured [21 and 22].

2.4 Determination of the joint strength

In contrast to ASTM standard D 1344 the size of the test surface of the cross-lap specimens is reduced, whereas the thickness of the glass body is increased (length 24, width 15.5, thickness >6 mm). This reduces the frequency of glass fracture in the tensile test. Before the compound specimens can be prepared, the rectangular glass bodies have to be polished on one side. The thermoplastic polymer is placed between the two polished glass plates. This "sandwich" is heated and the plastic melt creates an interface against the glass. In order to achieve an optimal compound, the temperature has to be adapted to the specific viscosity of the polymer. As far as polymer sheets like polyvinyl chloride (PVC) and polyvinyl butyral (PVB), which are used for intermediate layers in laminated safety glass, are concerned, an additional pressure of 2 MPa is required uniaxially.

The resulting cross-agglutinated compound specimens are pulled apart at a speed of 1 mm/min by two pegs in a draw unit (figure 3). The compound strength can be defined as required pressure in relation to the test surface (15.5×15.5 mm²). The mean is calculated out of 10 single measurements.

Alternatively, an additional joining process is applied for polymethyl methacrylate (PMMA) and polystyrene (PS). Following this process, the solution of these polymers is prepared and glass body specimens are cross-agglutinated with this viscous liquid. In order to evaporate the solvents the joined specimens are dried at 303 K

(30°C) for two days. The solvents are composed of 3.5 g PMMA dissolved in 10 ml chloroform (CHCl₃), and 5.0 g PS dissolved in 10 ml toluene (C₆H₅-CH₃), respectively.

3. Results and discussion

3.1 Surface energy of polymers

Numerous wetting tests were evaluated by applying equations (6 and 9). The resulting surface energy parameters of the polymers have been entered in table 5. It is noticeable that there is only a slight variation in total surface energy γ_i^{ges} , i.e. between 32 and 43 mJ/m². But as far as the polar part of the surface energy γ_i^p is concerned, significant differences can be recognized. Low-density polyethylene (LDPE) and polypropylene (PP) show a polarity that is not worth mentioning. These polyolefins can be classified as non-polar because they do not have any polar groups in their molecular structure. If, however, polar groups exist in plastics (e.g. the carbonyl group in PMMA), this goes along with higher results of γ_i^p . Polyamid (PA-6), which forms hydrogen bonds between the molecular chains, is characterized by the highest polarity (8.3 mJ/m²). It is surprising that the polarity of PVC is rather low according to this evaluation.

On the right-hand side of table 5 the results of the acid-base evaluation are represented. A comparison shows that the newly introduced surface energy amount as a consequence of acid-base interactions γ_i^{AB} replaces the polar amount of the surface energy γ_i^p . This means that the interactions have the same cause. The difference merely consists in different interpretations of the causes of the forces that are at work. According to the acid-base approach attracting forces are not only caused by unspecific dipole interactions. What is far more important is the type of functional group, i.e., whether it is an electron donator (basic) or an electron acceptor (acid). Accordingly interactions are only possible if the acid components of the first agent interacts interfacially with the basic one of the second agent [10].

The last two columns of table 5 show the acid and base parameters of the surface energy γ_i^{\oplus} and γ_i^{\ominus} as a result of an analytical evaluation of the contact angle measurements (equation (9)). In accordance with other analyses the base parameter is high, whereas the acid parameter is rather low [23 and 24].

This is why it creates difficulties for the interpretation of the ascertained quantities. A direct comparison, however, reveals that the behaviour of PMMA is more basic than the average of the other polymers. This result is in line with other measurements of infrared spectral shifts that prove the basicity of this polymer [7]. With regard to structure this behaviour can be traced to the proton-accepting effect of the carbonyl groups (C=O). Polystyrene also shows a basic behaviour. This result has been already obtained earlier [25]. Unlike the behaviour of all the other polymers the behaviour of PVC is rather

Table 5. Surface energy parameters determined by the "three-liquid method" and comparison with the evaluation of the geometric-mean equations in mJ/m²

polymer	γ_i^{ges}	γ_i^{d}	γ_i^{p}	γ_i^{LW}	γ_i^{AB}	γ_i^{\oplus}	γ_i^{\ominus}
	geometric-mean equation			acid-base analysis			
LDPE	33.4	33.4	0	33.4	0.5	0.05	1.60
PP	32.9	32.7	0.2	32.7	0.4	0.02	1.35
PS	36.7	36.2	0.5	36.2	1.3	0.09	4.37
PBTP	39.1	37.6	1.5	37.6	0.6	0.01	10.67
PMMA	40.8	38.6	2.2	38.6	3.1	0.16	14.89
PA	42.9	33.6	9.3	33.6	8.3	1.27	13.68
PVB	39.4	36.4	3.0	36.4	2.5	0.12	12.25
PVC	39.3	39.3	0.01	39.3	3.1	0.38	6.47
TPU	37.9	36.3	1.6	36.3	1.0	0.02	14.56
PES	40.7	35.6	5.1	35.6	4.7	0.90	6.07

acidic, which is confirmed by earlier tests [7]. In contrast with comparative figures in expert literature, the analysis of polyvinyl butyral (PVB) shows a rather basic behaviour [26].

In conclusion it can be pointed out that polymers can be sufficiently characterized by their surface energy or by their total acid-base affinity. It has to be stressed that the capacity for acidic and basic interactions can not be exactly quantified, but that there are tendencies noticeable as a result of the applied method. Other methods lead to more exact results, but their technical feasibility is more difficult to achieve [6].

3.2 Surface energy of glasses

New surfaces are created if a Vickers diamond causes indentations as well as radial cracks on smooth glass surfaces. The corresponding energy required is regarded as energy of fracture or as effective surface energy γ_{eff} . As for the state of elasticity, there exists the following correlation between the stress intensity factor K_{Ic} and the effective surface energy

$$\gamma_{\text{eff}} = \frac{K_{\text{Ic}}^2}{2E} (1 - \nu^2) \quad (10)$$

with E = Young's modulus, ν = Poisson's ratio. The stress intensity of the glass can be obtained by measuring out the indentation diagonal (2a) and the total length of crack (2c), and if the load P is given [20]:

$$K_{\text{Ic}} = 0.036 \cdot E^{0.4} P^{0.6} a^{-0.7} (c/a)^{-1.5} \quad (11)$$

The results of the analysis according to the Vickers method are represented in line 1 of table 6. They are ranging between 2300 and 6100 mJ/m². A load of 2.94 N corresponds with a loading duration of 30 s (exception: aluminosilicate glass: 9.81 N).

If these figures are compared with the ones measured and calculated in connection with glass melts (table 6), it becomes plain that these results are on a lower scale. This statement can also be held up if an additional temperature coefficient is determined and if one formally extrapolates these figures to room temperature. Between 1200 and 1500 K a temperature coefficient of $-0.048 \text{ mN} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ is measured for float glass. At room temperature this would result in a surface energy of 410 mJ/m². It becomes apparent that the fracture (Vickers method) requires further high energy amounts e.g. for plastic deformation. Nevertheless it can be concluded from the results that there are clear differences between the various glasses. Thus, a lower surface energy can be attributed to lead silicate glass because of the high lead content. Aluminosilicate glass has a higher surface energy owing to the great number of network formers.

Another problem consists in the estimation of the surface energy state with regard to the real glass surface at room temperature. The highly energetical glass surface is transformed into a low-energy glass surface by chemisorption (formation of silanol groups) and by an additional adsorption of water [28]. This can be derived from the known wetting behaviour, which depends on ambient humidity. However, in dry air a critical surface tension of merely 75 mN/m [29] is obtained. This is the value by which the wetting behaviour of the substrate is characterized.

In conclusion it can be pointed out that it is impossible to describe the surface energy state of glass under real conditions.

3.3 Wetting behaviour of thermoplastic polymers on glass surfaces

3.3.1 Contact angle

It is impossible to directly determine the work of adhesion via the surface and interfacial energies of the participants and by employing equation (1). This failure is

Table 6. Comparison of the surface energies of technical glasses, measured at 293 and 1400 K, calculated at 1173 K in mJ/m²

	lead silicate glass	TV glass (screen)	float glass tin-side	E-glass	aluminosilicate glass	basalt glass
Vickers method at 293 K	2350 ± 150	3370 ± 210	4900 ± 480	5690 ± 320	6050 ± 390	6090 ± 630
cylinder method at 1400 K	225	—	355	—	—	—
calculated from [27] at 1173 K	192	318	340	392	392	424

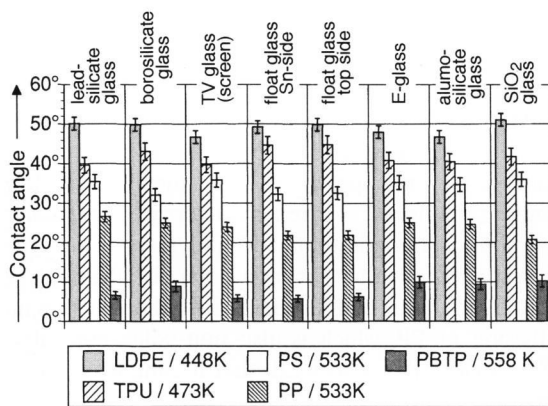


Figure 4. Contact angle of polymer melts on different glass surfaces.

due to the fact that the physical quantities of glass can not be reliably ascertained (see also above). In order to obtain further information on interactions between compound partners, the measurements of contact angles formed by thermoplastic polymers on glass surfaces may be helpful. Apart from that the wetting behaviour is a decisive parameter for numerous technical processes.

The results of the contact angle measurements are shown in figure 4. It is the (apparent) final angle that is measured. The contact angles vary between 6° for PBTP (nearly complete wetting) and 50° for LDPE. Most of the polymers do not show complete spreading.

In figure 4 is demonstrated that the glass composition does not significantly influence the wetting behaviour of the polymers. This result is indeed of great relevance in technology, e.g. for laminating glass. In the following the influence of viscosity is examined in order to have a closer look at the wetting behaviour of thermoplastic polymers.

3.3.2 Kinetics of the wetting process

Below, the time dependence of the wetting angles of the polymer melt is observed on a glass substrate. Figure 5 serves an illustration of how the contact angle of polypropylene (PP) advances on different glasses at a constant temperature of 533 K. Using a double-logarithmic expression the exponent p in the angle's time dependence

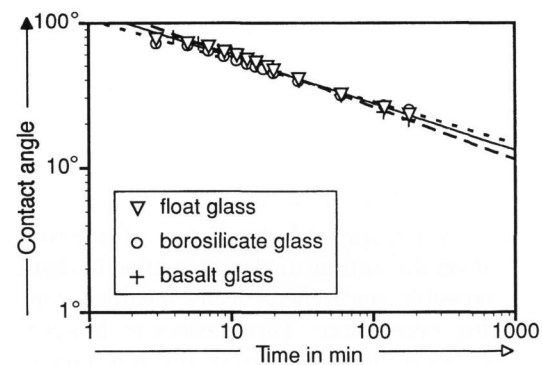


Figure 5. Spreading of polypropylene (PP) on three different glass surfaces at a constant temperature of 533 K.

can be read from the gradient of the straight line (equation (13)). From the spreading laws concerning low viscous liquids [30 and 31] the spreading exponent $m = 3$ was obtained by experiment. And a value of 0.3 for the exponent p can be obtained on the assumption of a symmetric drop (equations (12 and 13)),

$$U \sim \frac{\gamma}{\eta} \cdot \theta^m \quad (12)$$

for $\theta \ll 1$,

$$\theta \sim t^{-p} \quad (13)$$

for $\theta \ll 1$.

This means that the double-logarithmic expression reveals that the time curve of the wetting angle seems to be equivalent to the straight line which has a gradient of p . A linear dependency does indeed exist, which can be seen in figure 5. Thus, the validity of equation (13) is proved.

In all cases the exponent p varies between 0.29 and 0.36. It can be proved that within the scope of measuring accuracy the type of glass is independent of spreading kinetics. This is exemplified by the different glasses in figure 5. Such a linear curve is true for all the polymers examined, the spreading exponents, however, are, polymer-specific. In spite of long time tests no decrease in slope was noticeable. It is impossible to obtain a limit for the wetting angle which would be equivalent to an

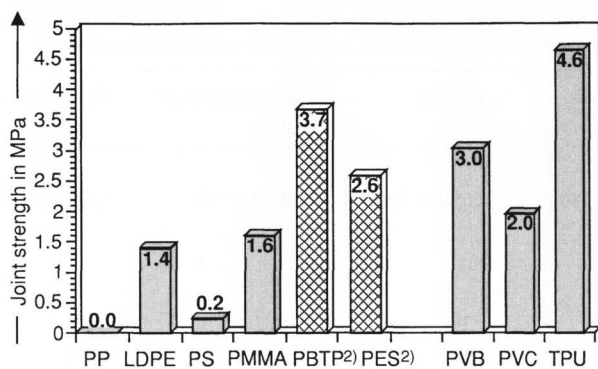


Figure 6. Joint strength of float glass (top side) combined with different thermoplastic polymers. ²⁾ glass cohesion failure.

equilibrium. Complete spreading is only reached in unrealistic periods of time (≥ 1000 min). It is, however, noticeable that it only apparently comes to an equilibrium, since there is a slowdown in the motion of the drop.

A direct determination of the energy of adhesion (equation (2)) via the wetting angle represented in figure 4 is not permissible since energetically regarded complete spreading takes place. This process is, however, very slow because of the high viscosity. It can be noticed that the wetting angle, which is being formed during a certain amount of time, is directly dependent on the viscosity of the thermoplastic polymer and is not dependent on the glass composition.

Such a course of wetting is not only noticed for viscous liquids but is also known through contact angle measurements of glass on ceramic substrates. If the viscosity is higher than 10^4 dPa s, the motion of the drop decreases along with decreasing wetting angles, so that there only seems to be an equilibrium.

3.4 Results of adhesion measurements

3.4.1 Strength of compounds between glass and thermoplastic polymers

The cross-lap tensile method is used in order to examine the real conditions of joint strength with regard to compounds between glasses and polymers. Adhesion is achieved by melting a thermoplastic polymer between two smooth glass bodies. The values obtained vary between 0 and 5 MPa (figure 6). Whereas the adhesion of polymers with low polarity like LDPE, PP and PS is not very strong, polymers with polar groups lead to greater compound strength. Macroscopic cohesion failure – mostly inside the glass – is true for stiff thermoplastics PBTP, PES and PA-6. Unsymmetrical tensile stresses can be avoided by polymers with a low Young's modulus. This is the result of a mathematical determination of stress conditions. According to this calculation the highly elastic polymers PVB, PVC and TPU show high compound strength and macroscopic adhesion failure.

On account of their different properties the polymers cannot be compared. Nevertheless, important conclusions can be drawn from the results.

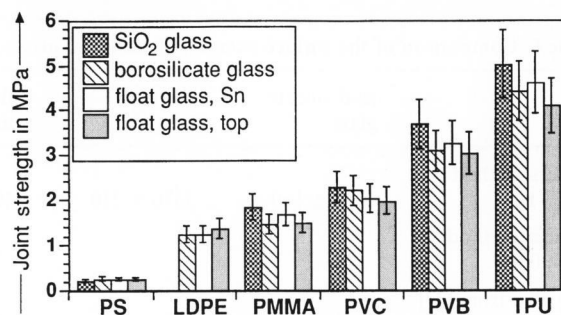


Figure 7. Joint strength between thermoplastic polymers and different glasses.

- The adhesion of polar polymers (table 5) on glass surfaces is stronger than the adhesion of non-polar polymers.
- Those polymers which are able to contribute to a reduction of stress peaks – since they have a low Young's modulus – are characterized by greater compound strength than stiff polymers. Thus, the corresponding value for non-polar LDPE with a Young's modulus of 150 MPa is 1.4 MPa, whereas an adhesion of PP, which is also non-polar but stiffer ($E = 1600$ MPa) is so weak that it cannot be measured.
- Since glass is highly sensitive to tensile stress, glass fracture is caused even by low load if stiff polymers with strong adhesion (PBTP, PES, PA-6) are used. This is the reason why highly elastic sheets (such as PVB and TPU) are widely applicable although they are not so strong.
- At room temperature some polymers are below their glass transition temperature T_g (PS, PMMA, PBTP, PA and PES). Here there may be thermally induced stresses, that reduce the compound strength. This is a consequence of cooling after the heat of the joining process.

3.4.2 Influence of glass composition

The different glass compositions, however, do not have any significant influence on the stress condition, so that the influence on compound strength can be determined. Although the silicate glasses differ very much in surface energy, the results achieved are quite similar (figure 7). Systematic differences between float and E-glass cannot be observed either. A 20% lower strength of adhesion can be attributed to lead-containing glasses, whereas the values for pure SiO₂ glass are above average. On the whole, the differences are small.

3.4.3 Role of acid-base interactions

In order to examine the influence of specific acid-base interactions on specific interfacial adhesion, glasses that differ in alkali/alkaline earth content – and thus with levelled basicity – are produced. These glasses are joined by heat with polymers of which the acid-base affinities are known.

Slight compound strength is achieved by PS (figure 8). What is surprising is that there is no adhesion between the slightly basic polystyrene and the basic glass G 55 (55 wt% SiO₂). The adhesion properties of PMMA on glasses, which are rich in SiO₂ and which are therefore acidic, are well developed. Besides that it becomes obvious that adhesion is possible on the basic glasses G 55 and G 65.

Acidic PVC on pure SiO₂ is characterized by the lowest level of adhesion, i.e. 2.5 MPa (figure 8), whereas the level of adhesion is higher as far as alkali or alkaline earth-containing glasses are concerned. With PVB it is just the other way around. Here the highest level of adhesion is reached on an SiO₂ glass surface. But the differences are insignificant, with a variation coefficient of approximately 10%. The basic surface property of PVB is now being confirmed by these results.

Another possibility to achieve a required mobility for the formation of interfaces results from dissolving the polymer in a solvent. Therefore, the thermoplastic polymers polystyrene and polymethylacrylate are dissolved in chloroform (PMMA) or in toluene (PS). The joining of the glass pieces with the viscous solution and the evaporation of the solvent result in compound strength levels that are represented in figure 9. No adhesion could be noticed between PMMA and G 55 and G 65 glasses, as even slight use causes a peeling off of the polymer film. As for G 80 and SiO₂ glasses, the compound strength is on the same level as compound strengths achieved by using hot-melt adhesives (figure 8). As a consequence basic PMMA adheres only to acidic glasses.

However, it has to be taken into account that chloroform is an acidic solvent which covers the basic glass surface by adsorption [32]. Thus, the formation of an interface between PMMA and glass is avoided in those cases.

The application of dissolved polystyrene on glass attributes greatly to its compound strength. As compared with figure 8, figure 9 shows an increase in strength by 0.2 to 0.6 up to 1 MPa. It can be derived that the application of a polymer in solution provides a technical alternative to joining thermoplastics and glass by heat, so that thermal stress is avoided.

PS is dissolved in only slightly basic toluene [33]. Obviously, this does not prevent the slightly basic polystyrene from adsorbing to the rather acidic glasses G 80 and SiO₂, as these combinations result in the highest levels of compound strength.

Thus, the compound strength of both basic polymers in solution, which were joined to the glass specimens, is definitely dependent on glass composition, especially with regard to acidity and basicity of the glass. Since it is difficult to exactly quantify the polymer solution that was used in the joining process, this method shows a rather great mean variation, which may be an explanation for the unusually high value of PMMA for

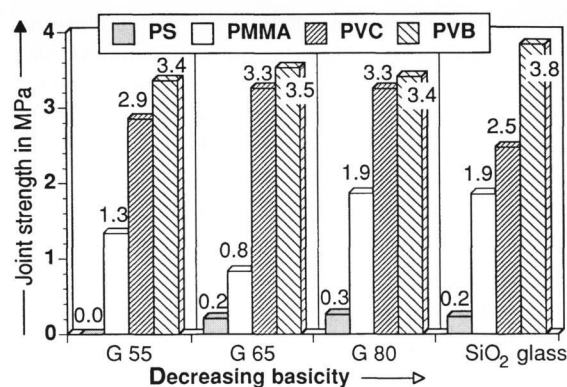


Figure 8. Joint strength between thermoplastic polymers and glasses of different basicity (joining with heat by melting the polymer).

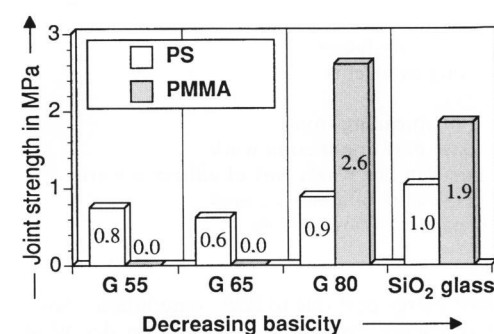


Figure 9. Joint strength between polystyrene (PS) and polymethyl methacrylate (PMMA) from solution and glasses of different basicity.

G 80 glass; G 55 and G 65 glasses, however, showed no measurable adhesion at all, although far more than 40 specimens were tested.

4. Summary

The thermodynamic work of adhesion cannot be determined by wetting measurements of polymer melts on glass. Although a finite contact angle can be noticed, an analysis of spreading kinetics shows that an energy equilibrium is represented by complete wetting. The motion of the spreading front is determined by the viscosity of the polymer melt. It was proved that the composition of silicate glass does not influence the wetting behaviour of polymers, although the materials differ in view of their surface energy.

Moreover, a direct determination of work of adhesion is impossible, as the characterization of surface energy on real glass surfaces is problematic. The theories on wetting and adhesion, however, can be successfully used for characterizing the surface energy and polarity or acid-base affinity of the polymers. To know about these properties is very helpful for the interpretation of the results, as is proved by the adhesion strength tests.

Since it cannot be attained to use the adhesional work as a measure of adhesion, the determinants have to be regarded separately. Non-polar polymers show a low level of adhesion on glass surfaces. Mechanical and thermal properties of the polymers play a critical role. Here the ability to relieve stress by expansion is of great importance. Compound strength, however, is scarcely dependent on glass composition.

If a polymer in solution is applied, the surface property (acid-base affinity) of the glass plays a dominant role, and it may be that adhesion fails completely. It is competitive adsorption between the polymer and the solvent on the glass surface that may be responsible for the failure.

5. Nomenclature

a	indentation diagonal
c	total crack length
E	Young's modulus
K_{Ic}	stress intensity factor
m, p	spreading exponents
t	time
U	speed of spreading front
$W^{Ad,AB}$	acid-base part of adhesion work
$W^{Ad,LW}$	Lifshitz-Van der Waals part of adhesion work
$W^{Ad,d}$	dispersive part of adhesion work
$W^{Ad,p}$	polar part of adhesion work
γ	surface energy
γ^{AB}	surface energy part due to acid-base interactions
γ^{LW}	surface energy part due to Lifshitz-Van der Waals forces
γ^d	dispersive part of surface energy
γ^p	polar part of surface energy
γ^{\oplus}	acid parameter of surface energy
γ^{\ominus}	base parameter of surface energy
γ^{eff}	effective surface energy
γ_{LV}	surface tension of a liquid in contact with vapour
γ_{SL}	interfacial energy between a liquid and a solid surface
γ_{SV}	surface tension of a solid in contact with vapour
γ_{α}	surface energy of phase α
γ_{β}	surface energy of phase β
$\gamma_{\alpha\beta}$	energy at the interphase between phases α and β
η	viscosity
Θ	wetting angle
ν	Poisson's ratio

*

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