

WETTABILITY AND INTERPHASE ADHESION OF MOLTEN THERMOPLASTICS ON GLASS FIBRES

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ABSTRACT

Direct contact angle measurements were performed between different molten thermoplastics, polypropylene (PP), polyvinylidene fluoride (PVDF), and maleic anhydride-grafted polypropylene (MAPP), on smooth glass fibres and smooth glass plates. The matrices were selected as model systems for the investigation of the fibre–matrix interphase, based on the difference in surface energies between PP and PVDF (physical interactions) and the effect of chemical bonding between PP and MAPP. In this way, physical and chemical adhesion were studied independently. The mechanical strength of the interfaces was then assessed by single fibre pull-out tests. The interfacial strength and the wettability of molten thermoplastics correspond well to the predictions based on the calculation of the theoretical work of adhesion between the matrices and the fibre surfaces for PP and PVDF; however, the wetting behaviour of molten MAPP is affected by the MA content if compared with the surface energy analysis made at room temperature. The hypothesis is that the wetting behaviour of molten MAPP is mainly related to chemical interaction of MA groups with the glass surface rather than a variation in surface energy.

1 INTRODUCTION

The importance of the interphase as the material part for transferring stress is widely recognized [1]; however, the wetting behaviour of molten polymers during composite manufacturing or how the interface is formed at high temperature between the molten thermoplastic and the hot fibre surface are yet to be studied in detail. The final mechanical properties of composite materials are highly dependent of the interaction between fibres and polymer matrices since the load distribution efficiency at the interphase is determined by the degree of adhesion between the components [2]. This strong fibre-matrix adhesion has to be obtained by interfacial interactions, including mechanical interlocking, chemical bonding and physical mechanisms of adhesion.

If the matrix is not able to fill irregularities at the fibre surface, the area of contact between the fibre and the matrix will be reduced, producing in turn, a reduction in adhesion. On the other hand, if the matrix can fully wet the rough surface, mechanical interlocking and increased contact area will lead to increased adhesion.

Chemical adhesion also depends on the degree of wetting that provides intimate contact between both phases. Then covalent bonds can be formed across the interface when atoms at the fibre surface share electrons with matrix atoms, producing bonds with very high strength.

The fibre surface is also able to interact with the matrix without undergoing covalent bonding. These interactions arise from physical forces and predominantly control the wettability of the liquid polymer on the fibre surface [3], as well as the adhesion in a typical thermoplastic composite. The study of physical interactions is crucial for obtaining a better interphase, since the other mechanisms of adhesion depend on a good physical interaction.

The common procedure to evaluate these physical interactions in thermoplastic composites is to estimate the fibre and matrix composition in terms of surface energy components, utilizing the results of contact angle measurements of probe liquids on both the fibre and the matrix in solid state at room temperature [4, 5]. In this study, contact angles of molten polyvinylidene fluoride (PVDF), polypropylene (PP) and molten maleic anhydride-grafted polypropylene (MAPP), on smooth glass fibres and smooth glass plates, were measured as a direct indication of the level of adhesion that could potentially be obtained in the final composite. These values were then compared to those obtained by measuring contact angles with different reference liquids using the i) Wilhelmy technique on solid matrix films and fibres, and ii) by applying the acid-base theory for calculating the surface energy components. The matrices were selected as model systems for the investigation of the fibre–matrix interphase, based on the difference of surface energies between PP and PVDF and the effect of chemical bonding between PP and MAPP. The surface energies of the molten thermoplastics were determined by the pendant drop method and the interphase composition was analysed by ToF-SIMS and FTIR spectroscopy. Finally, in order to correlate the real strength of the interphases with the theoretical work of adhesion, the fibre-matrix interphase bond strength was characterised by the critical local value of interphase shear stress obtained by single fibre pull-out tests.

2 MATERIALS AND METHODS

2.1 Materials

Glass slides were normal cover glass used for optical microscopy (Sigma-Aldrich) with a cross sectional area of 24mm x 22mm, which were cut into 5mm x 5mm for this study. Glass fibres (diameter: 200 μm) were obtained from the core of Thorlabs optical fibre (FR200UMT).

Polypropylene (PP) 515A with a melt flow rate of 24 g/10 min (230°C/2.16 kg), and density of 0.905 g/cm³ was obtained from Sabic (Germany). 7% maleic anhydride grafted polypropylene (MAPP) Licocene 6452 with viscosity of 1100 mPa.s (170°C), and density of 0.93 g/cm³ was supplied by Clariant (Germany).

2.2 Materials preparation

Only the silica core of the optical glass fibres is needed, and thus the outer layers have to be removed. The cladding layer is removed by submerging the stripped fibres in hot sulphuric acid. The fibres were submerged in piranha solution (mixture of concentrated sulphuric acid and hydrogen peroxide) for 30 minutes. Finally, the glass fibres were rinsed off with water and stored in ultrapure water (resistivity > 18M Ω .cm) for avoiding environmental organic contamination. Glass slides were also cleaned under the same procedure.

2.3 Contact angle measurements and surface energy analysis

Advancing and receding contact angles of various test liquids (ultrapure water: 18.2 Ω cm resistivity, diiodomethane: Merck, and ethylene glycol: Sigma–Aldrich) were measured on the polymer films and glass fibres under controlled conditions (temperature of 20°C and humidity of 50%), with a Krüss K100 tensiometer using the Wilhelmy technique [5, 6]. In order to better describe both the low surface energy and the high surface energy components of the analysed surfaces, the average of the cosines of the advancing (θ_{adv}) and receding (θ_{rec}) angles was used for the glass fibres to estimate the cosine of the equilibrium angle (θ_{equ}), as has been suggested by Andrieu et al.[7], and is shown in Equation 1.

$$\cos\theta_{equ} = 0.5\cos\theta_{adv} + 0.5\cos\theta_{rec} \quad (1)$$

Surface energy components were calculated according to the Van Oss model and by using the SurfTen 4.3 software developed by Claudio Della Volpe [8]. Also, the work of adhesion (W_a), the spreading coefficient (S), the wetting tension (ΔF), and the interfacial energy (γ_{st}), which are wetting parameters related to the interfacial strength [9], are calculated according to the following equations:

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} = \gamma_l (1 + \cos \theta_{\text{equ}}) \quad (2)$$

$$S = \gamma_s - (\gamma_l + \gamma_{sl}) = \gamma_l (\cos \theta - 1) \quad (3)$$

$$\Delta F = \gamma_s - \gamma_{sl} = \gamma_l \cos \theta_{\text{equ}} \quad (4)$$

$$\gamma_{sl} = \left(\sqrt{\gamma_s^{\text{LW}}} - \sqrt{\gamma_l^{\text{LW}}} \right)^2 + 2 (\sqrt{\gamma_s^+} - \sqrt{\gamma_l^+}) (\sqrt{\gamma_s^-} - \sqrt{\gamma_l^-}) \quad (5)$$

Where γ_{sl} represents the surface energy (solid and liquid respectively), γ_s^{LW} represents the Lifshitz-van der Waals component, $\gamma_{s,l}^+$ represents the acidic, and $\gamma_{s,l}^-$ the basic component.

The polymers are molten in a Ramé-hart environmental chamber with controlled inert gas environment to avoid degradation at 200°C. For measuring the contact angle of a molten polymer on a fibre, the latter is gradually introduced into a liquid polymer until the meniscus is formed, and then its contour shape is fitted with the Young-Laplace equation to calculate the contact angle.

For analysing the wetting behaviour of the molten thermoplastic on a flat surface, a droplet is formed with the liquid thermoplastic and the contour shape is also fitted with the Young-Laplace equation.

2.4 Pull-out test

A block of polymer was put in an aluminium cylindrical container with a radius of 5 mm and heated until the melting temperature. When the polymer was completely molten, the fibre was placed perpendicularly to the polymer surface and in it was centred with the help of an optical microscope to guarantee accuracy.

The evaluation of the interfacial debonding strength, τ_d , and the interfacial friction, τ_f , was made by following the procedure developed by Zhandarov et al. [10, 11], and the methodology can be consulted in our previous publication [4].

2.5 Surface tension measurement

An elevated temperature syringe chamber in combination with the Ramé-hart environmental chamber (see section 2.3) with controlled inert gas atmosphere were used to produce stable molten polymer axisymmetric drops, which were hanging from a metal needle at 200 °C inside the chamber.

The shape of the drop was analysed (see Figure 1) and then fitted with the theoretical profile obtained according to the Young-Laplace equation by the Pendent_Drop software [12]. Figure 1 shows the time evolution of surface tension of a typical liquid MAPP pendant drop at 200°C. For a correct surface tension measurement the curvature of the drop needs to vary significantly [12, 13]. The surface tension values reported in this publication corresponds to the average of the values of the stable zone (between 800 and 1200 seconds for Figure 1), where the surface tension and volume are stable. After the stable zone, the drop is close to pinch-off (after ~1200 seconds) and volume starts to increase, as well as the RMS value. Then, the surface tension values are not reliable anymore.

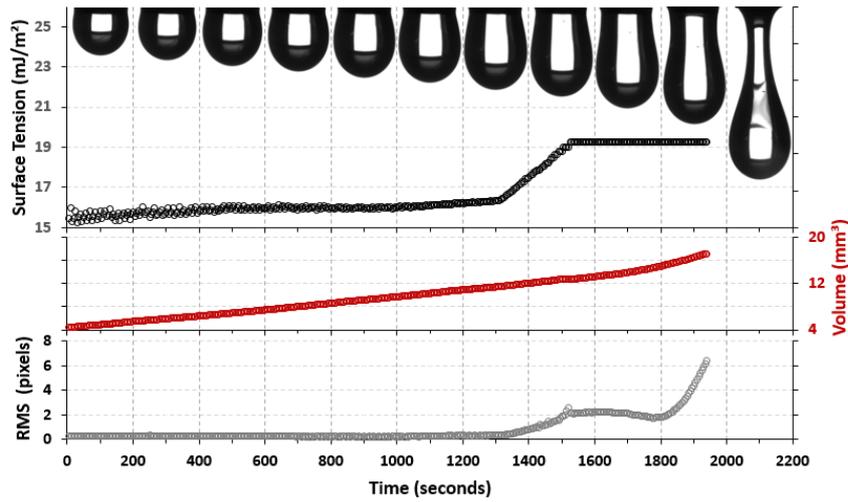


Figure 1. Surface tension, volume and root-mean-square (rms) deviation of the fit for a drop of molten MAPP as function of time.

2.6 Image acquisition

Samples were imaged using a Motic SMZ-171-TH microscope and a 3664x2748 pixel Moticom camera. The resolution of the imaged surface was $0.213 \mu\text{m}/\text{pixel}$ for the contact angle measurements and $0.134 \mu\text{m}/\text{pixel}$ for the pendant drop method. The picture interval was fixed to 1 second with an exposure time of 700 ms.

3 RESULTS AND DISCUSSION

Table 1 shows the advancing, receding, and equilibrium contact angles. The latter were used for the calculation of the surface energy components of the thermoplastic surfaces, which are shown in Table 2. As expected, PVDF possesses higher acidity due to the different electro-negativities of carbon, fluorine, and hydrogen. In particular, the strong inductive effect of the fluorine atoms polarizes the electronic distribution of partially fluorinated polymers [14].

For the case of PP, we find a deviation in the magnitude of the polar surface energy component, which was expected to be zero since pure PP is a nonpolar polymer. This effect could be related to aging processes or surface contamination [15]. For the case of MAPP, the determined surface energy shows an increment of polar components possibly due to the presence of maleic anhydride [15].

liquid	PP			MAPP			PVDF		
	adv	rec	equ	adv	rec	equ	adv	rec	equ
WT	97.8 ± 1.6	74.1 ± 1.5	86.0 ± 1.1	99.7 ± 1.3	64.2 ± 0.9	82.3 ± 0.8	85.5 ± 0.9	68.9 ± 1.2	77.3 ± 0.7
EG	71.1 ± 0.6	49.4 ± 1.7	60.8 ± 0.8	84.8 ± 1.3	41.7 ± 0.8	65.3 ± 0.8	54.1 ± 1.2	32.1 ± 1.6	44.2 ± 0.9
DIO	67.9 ± 1.2	46.1 ± 1.7	57.7 ± 1.0	77.9 ± 0.9	38.1 ± 0.5	60.1 ± 0.5	63.6 ± 0.4	46.5 ± 1.8	55.5 ± 0.8

Table 1: Advancing, receding and equilibrium contact angles of probe liquids on thermoplastic surfaces: water (WT), ethylene glycol (EG), diodomethane (DIO).

Material	γ^{tot} (mJ/m ²)	γ^{LW} (mJ/m ²)	γ^{ab} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)
Glass	40.5 ± 2.1	29.7 ± 0.2	10.9 ± 0.2	1.1 ± 0.2	27.3 ± 0.1
PP	30.9 ± 0.5	29.9 ± 0.5	1.0 ± 0.2	0.1 ± 0.0	2.0 ± 0.3
MAPP	29.1 ± 0.4	28.5 ± 0.3	0.6 ± 0.2	0.0 ± 0.0	3.7 ± 0.3
PVDF	34.6 ± 0.5	31.2 ± 0.5	3.5 ± 0.2	0.9 ± 0.1	3.3 ± 0.2

Table 2: Surface energy components of glass fibre and thermoplastic films.

The work of adhesion, spreading coefficient, wetting tension, and interfacial energy for glass fibre as substrate were calculated for the various polymers by using equations 2,3,4 and 5 respectively (see Table 3).

Material	W_a (mJ/m ²)	S (mJ/m ²)	γ_{st} (mJ/m ²)	ΔF (mJ/m ²)
PP	66.00 ± 0.99	4.26 ± 0.99	5.37 ± 0.35	35.13 ± 1.30
MAPP	62.66 ± 0.65	4.46 ± 0.65	6.94 ± 0.13	33.56 ± 0.25
PVDF	70.76 ± 0.76	1.48 ± 0.76	4.38 ± 0.28	36.12 ± 0.36

Table 3: Wetting parameters with glass fibre as the substrate.

The results for PP and MAPP present a relatively low W_a and ΔF (if compared with PVDF) due to their almost zero polar component. It has to be noted that these values are only related to intramolecular physical forces and do not relate to covalent bonding (which is important in the case of MAPP).

On the other hand, PVDF shows a higher W_a than PP and MAPP, as well as a positive S value and a low γ_{st} , helping to achieve a good wetting of the molten polymer on the glass fibre. Furthermore, the ΔF value is the highest corresponding to the situation where W_a is maximum within the region where spontaneous wetting occurs [16]. This strong interfacial interaction is a consequence of electron donor-acceptor interactions due to the presence of a relatively high acidic component in PVDF and a high basic component on the glass fibre's surface; as well as a relatively high total surface energy of both the matrix and the substrate. Since polar interactions are electron donor-acceptor interactions, strong interfacial interactions occur only when one phase has basic and the other has acidic sites.

There was a good correlation between the interfacial parameters determined from the pull-out test and the theoretical W_a for glass as substrate. As it can be seen in Table 4, the value of τ_d for the PVDF-glass fibre system is approximately 5 times higher than the values obtained for the PP-glass system. The latter clearly indicates a higher interfacial adhesion and greater surface energy components compatibility of PVDF on glass fibres if compared with the PP system.

Matrix	τ_d (MPa)	τ_f (MPa)	W_a (mJ/m ²)	γ^{tot} (mJ/m ²)
PP	7.9	2.9	66.0	20.2±0.8
MAPP	17.0	1.6	62.7	19.1±0.9
PVDF	37.0	1.4	70.8	26.2±1.3

Table 4: Interfacial parameters determined from the pull-out test. W_a from Table 3.

If the PVDF and PP glass fibre systems are compared, the obtained τ_f value for the PVDF is lower in case of PP (see Table 4). Even though the roughness of the fibres was the same for the 2 glass systems, the effect of friction is apparently lower for PVDF than for the PP system. This may be related to the difficulty of PVDF to spread on the glass surface due to its low spreading coefficient (see Table 3), reducing the amount of area in contact with the glass surface and also reducing the mechanical interlocking, as the matrix does not penetrate that well into the surface roughness.

Regarding MAPP, although the W_a is the lowest of the three polymers, the obtained τ_d is considerably higher than for PP. The reason is the chemical bonding formed between the anhydride groups from the polymer and the hydroxyl groups from the glass surface.

The adhesion at the interface of MAPP has improved with respect to PP through chemical bonding (higher τ_d) but the strength of MAPP is even lower than the strength of PP (55 MPa and 30 MPa for PP and MAPP respectively); therefore, with a stronger interface, the failure occurs in the matrix. This can be observed in the SEM images of already pulled-out fibres, where remnants of MAPP can be observed on the fibre surface (see figure 1). Even though, MAPP is chemically bonded to the glass fibre, the adhesion strength is not better than the one of the PVDF system due to matrix failure.

In order to compare whether the physical interactions of molten thermoplastics and hot solid surfaces correspond to those utilising the results of contact angle measurements of probe liquids on both the fibre and the matrix in solid state at room temperature, contact angles of molten PVDF, PP and PVDF on glass were measured (see Figure 2). As it can be seen in Table 5, the contact angles does not correspond well to our previous surface energy analysis for PVDF and PP at room temperature. However, due to its high surface tension (see Table 4), the PVDF melt still showed a high work of adhesion, comparable to those obtained by the other melts.

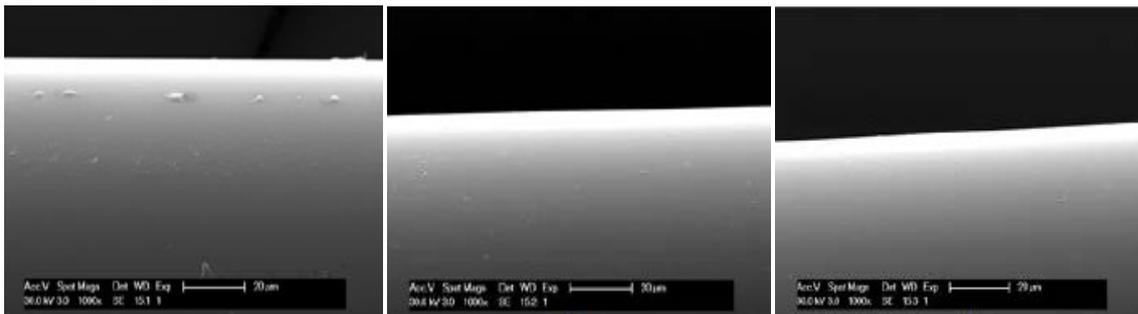


Figure 1: Pulled-out surfaces at the same magnification of MAPP (left), PP (center), PVDF (right).

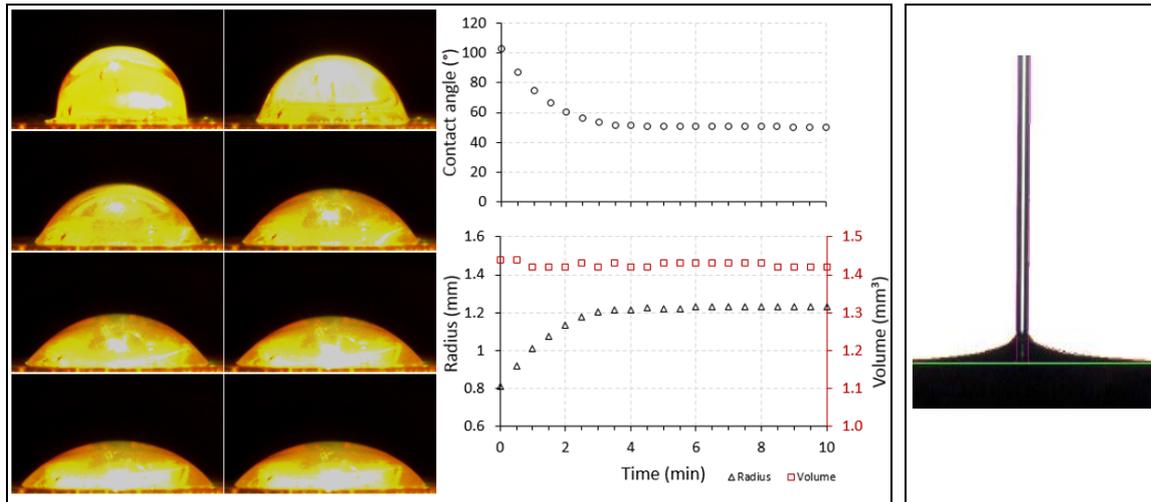


Figure 2: Contact angle, volume, and radius variation of molten MAPP on flat glass substrate (left), and the meniscus formation of molten PVDF on a glass fibre (right)

For the case of MAPP, although the total surface energy and their components are very similar to those of PP (see Table 2), its contact angle at 200°C is the lowest, and the explanation might be related to the chemical reaction of MA during the spreading process. The macroscopic spreading of a MA copolymer melt on a given substrate might be influenced by chemical interactions at the solid-liquid interface, obtaining lower contact angles if compared with systems without chemical interactions. On the other hand, the surface tension of molten MAPP is similar to the one of PP, indicating that the polar functional groups did not manifest itself in the surface tension. This suggested that chemical reaction releases additional free energy during the interfacial reaction and might be an additional driving force of wetting. The low contact angle of MAPP on glass corresponds well with the pull-out results, showing a higher τ_d for the MAPP-glass system even though the Wa at room temperature is lower than for PP (see Table 4).

Matrix	Fibre C.A. (°)	Surface C.A. (°)
PP	45.2 ± 1.8	49.9 ± 2.0
MAPP	20.3 ± 1.2	22.1 ± 4.3
PVDF	68.3 ± 1.9	70.6 ± 1.2

Table 5: Static advancing contact angles of molten PP, MAPP, and PVDF on glass substrate (glass and flat surface) at 200 °C.

4 CONCLUSIONS

The results revealed a direct correlation of the degree of wettability and the maleic anhydride (MA) content in molten MAPP, which seems mainly related to chemical interaction of MA groups with the glass surface rather than a variation in surface energy, since this remains relatively stable for MA and PP. Regarding practical adhesion, the critical interphase shear stress results show that the interphase strength in MAPP/glass was higher than in PP/glass as expected due to chemical bonding. However, the interphase strength in the PVDF/glass system was stronger than in MAPP/glass, although the direct contact angle measurement showed smaller contact angles for MAPP systems and despite the formation of chemical bonding between MAPP and glass. This result might be explained by the high surface energy of PVDF and by the fact that the MAPP/glass system fails in the matrix. In this case, the interfacial shear strength is limited by the shear strength of MAPP, which is relatively low.

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