Full Length Article

Wetting of polymer melts on coated and uncoated steel surfaces

Julie Vera [a], Elise Contraires [a], Anne-Catherine Brulez [a,b], Mathieu Larochette [a], Stéphane Valette [a], Stéphane Benayoun [a,*]

[a] Laboratoire de Tribologie et Dynamique des Systèmes, UMR CNRS 5513, Ecole Centrale de Lyon, 36 avenue Guy de Collongues, 69134 Ecully cedex, France
[b] Laboratoire de Génie de la Fonctionnalisation des Matériaux Polymères, Institut Textile et Chimique de Lyon, 87 chemin des Mouilles, 69134 Ecully cedex, France

ARTICLE INFO

ABSTRACT

A comparative study of the wetting of three different commercial polymer melts on various coated and uncoated steel surfaces is described in this report. The wettability of steel and coatings (three different titanium nitride coatings, TiN, TiNO$_x$, TiNO$_y$, a chromium coating, CrN, and a diamond-like carbon coating, DLC) used for mold in polymer processing is determined at different temperatures between 25 °C and 120 °C. Contact angle measurements of melted polypropylene (PP), Acrylonitrile Butadiene Styrene (ABS) and Polycarbonate (PC) on steel and on the different coatings were performed to investigate the wetting behavior under closer-to-processing conditions. Recommendations for good measurement conditions were proposed. Moreover, the surface free energy of each melt polymer was determined. The works of adhesion between all polymers and all substrates were established. Among all tested polymers, the lowest value of the works of adhesion is calculated for ABS and for PC thereafter, and the highest value is calculated for PP. These results will be particularly important for such applications as determining the extent to which these polymers can contribute to the replication quality in injection molding.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The control of wetting is a key factor in many engineering applications, including tribology and interface nanotechnology [1,2]. Knowledge of the surface tensions of molten polymers is important in many technological processes, such as wetting, adhesion, polymer blending and polymer injection [3–5].

Initially, research efforts were based on the study of the polymer melt. Most often, industrial polymers had been studied, such as polypropylene (PP), polyethylene (PE), and polystyrene (PS). Before 2000, numerous studies made valuable contributions to improving the knowledge of melted polymers. In particular, drop shape methods were an important step in understanding the surface (interfacial) tensions of melted polymers. These methods are based on the idea that the shape of the pendant drop is determined by a combination of surface tension and gravity effects. Despite the experimental simplicity of this method, the surface (interfacial) tensions of polymer melts must be determined with high precision. For example, in 1998, Axisymmetric Drop Shape Analysis was used by Kwok et al. [6] in order to study the surface tension of melted polymers at elevated temperatures. They used three polymers: polypropylene (PP), polyethylene (PE) and polystyrene (PS) at elevated temperature (above 170 °C). A decrease in surface tension was observed when the temperature increased.

More recently, studies had been conducted on different coatings used in plastic processing as chromium coating or DLC coating. Many studies aiming at understanding the effect of temperature on the surface free energy have been published over the last 15 years. Zhao et al. showed that the total surface free energy (SFE) and the dispersive component of the surface free energy of different DLC coatings, titanium and stainless steel decreased when the surface temperature was increased. However, the acid-base component of SFE increased with increasing temperature. Those experiments were performed at temperatures ranging from 20 to 95 °C [4]. All the results were given at low temperature (less than 120 °C). CrN$_x$ thin films are known for their excellent hardness, thermal stability and non-sticking properties (low surface free energy). Concerning Cr-based coatings, Chiu et al. [7] showed that Cr coatings with low an SFE could increase by more than 50% the number of molding injections before the mold is worn out. Another type of coating that is used in plastics processing is titanium nitride coatings. These coatings are known for their tribological properties and reasonable price [8].

Table 1
Test liquids and their surface tension components from [4,17–19].

Liquids	Temperature	Surface tension data (mN/m)		
		γ_L	$\gamma_L{}^d$	$\gamma_L{}^p$
Water, H_2O	25	72.8	21.8	51.0
	60	66.2	19.8	46.4
	95	59.9	17.9	42.0
Diiodomethane, CH_2I_2	25	50.8	50.8	0
	60	45.2	45.2	0
	95	40.5	40.5	0
	120	37.2	37.2	0
Ethylene glycol, $C_2H_6O_2$	25	47.3	28.6	18.7
	60	45.0	27.1	17.8
	95	42.6	25.7	16.9
	120	41.0	24.8	16.2

However, the relationship between the key parameters affecting the wetting of melted polymers under realistic injection conditions has not been thoroughly elucidated. The pendant and sessile drop methods are generally used in order to characterize the relationship. Recent studies, in the last 3 years, focused on understanding the role of the surface of the injection mold in the replication quality. These studies studied the interface between the molten polymer and the mold surface. First, in 2014, *Zhang and Al* compare the contact angle of four molten polymers (high density polyethylene, polypropylene, polycarbonate and cyclic olefin copolymer) deposited on four steel substrates with different roughness. They deduce that the roughness and melt temperature play an important role in the micro injection molding process [9]. In the same year, Bagcivan et al. studied the adhesion behavior between coatings and two different PMMA. In this purpose, they study the time evolution of contact angle between a pellet of polymer and their coatings. They concluded that there is a significant impact of the coatings on the contact angle [10]. Zitzenbacher et al. [11] compared the contact angle of molten PP, HDPE, poly(methyl methacrylate) (PMMA) and polyamide 6.6 (PA6.6) on steel and different coatings. They compared the contact angles with the SFE of the solid polymers. They showed that the wettability of PVD- and CVD- coatings with melted polymers is similar to that of steel. These coatings exhibited generally a high surface energy which causes a rather low contact angle. Rytka et al. [12] compared the quality of replication with the dewetting potential Ω_s. Indeed, as highlighted by Rytka et al., a higher works of adhesion (or spreading coefficient) between the polymer melt and the mold is supposed to induce a better filling of the structure [13,14]. Thanks to the wetting of polymers, we aim to predict the polymeric filling in the features of the mold. In this case, issues associated with the cooling of the polymer or demolding the solid part are not studied. However, a higher adhesion between the solid polymer part and the mold may cause the replica to be damaged or deformed during the demolding phase [15,16].

1.1. Theoretical background

To calculate the surface free energy (SFE) of a substrate, we need some parameters for liquids. Three tests liquids were used as a probe for the surface free energy calculations. The key properties of the selected liquids are presented in Table 1.

The surface tension of a liquid decreases with increasing temperature and vanishes at the critical point. There are semi-empirical relations found by Eötvös and later, Katayama and Guggenheim [20–22]. These equations depend on the nature of the liquid:

$$\gamma = \gamma^* \left(1 - \frac{T}{T_c}\right)^n \quad \text{or} \quad \gamma = \gamma^*(1 + \alpha T)^n$$

Where γ^* is a constant depending on the liquid, n is an empirical factor (depending on the liquids) and α is a constant.

The surface tension of distilled water between 20 and 95 °C was estimated using the following equation [4,19]:

$$\gamma_L = 235.85 \left(\frac{374 - T}{647.15}\right)^{1.256} \left[1 - 0.625 \left(\frac{374 - T}{647.15}\right)\right] \quad \text{(A.1)}$$

where T(°C) is the temperature of distilled water. The surface tensions of diiodomethane between 20 and 170 °C were estimated using the following equation [4]:

$$\gamma_L = 53.48 - 0.14154T + 4.9567 \times 10^{-5}T^2 \quad \text{(A.2)}$$

where T(°C) is the diiodomethane temperature. The surface tensions of ethylene glycol at 20–170 °C were estimated using the following equation [4,23,24]:

$$\gamma_L = 48.97 - \frac{T}{15}, \quad \text{(A.3)}$$

where T(°C) is the temperature of ethylene glycol. In three test liquid cases, the surface tension components of the test liquids at different temperatures were estimated by assuming the test liquid surface tension.

With these values, we could deduce the polar and the nonpolar components, assuming that their relative percentage does not change with the change of the temperature.

The surface free energy of solids may be determined by measuring the contact angles of liquids with known surface tension. The theory of the contact angle of pure liquids on a solid was stated first by Sir Thomas Young, two hundred years ago: "for each combination of a solid and a fluid, there is an appropriate angle of contact between the surfaces of the fluid, exposed to the air, and to the solid" [17]. The mathematical translation of this statement is the famous equation:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}, \quad \text{(A.4)}$$

where γ_L is the experimentally determined surface tension of the liquid, θ is the contact angle, γ_S is the surface free energy of the solid and γ_{SL} is the solid-liquid interfacial energy.

Fowkes [25], a pioneer in the surface free energy component approach, divided the total surface free energy in two components: the dispersive and polar components. The first component results from the molecular interaction due to London forces and the second component is due to all the non-London forces:

$$\gamma_i = \gamma_i^d + \gamma_i^p, \quad \text{(A.5)}$$

Owens and Wendt [18] extended the Fowkes equation and included a hydrogen bonding term. They used a geometric mean to combine the dispersive force and hydrogen bonding components:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d}\sqrt{\gamma_L^d} - 2\sqrt{\gamma_S^p}\sqrt{\gamma_L^p}$$

From the Young equation, it follows that:

$$\gamma_L \left(1 + \cos\theta\right) = 2\sqrt{\gamma_S^d}\sqrt{\gamma_L^d} + 2\sqrt{\gamma_S^p}\sqrt{\gamma_L^p}, \quad \text{(A.6)}$$

and $\gamma_S = \gamma_S^d + \gamma_S^p$ The objective of this research is to study the intensity of the chemical interactions between a polymer melt and coatings usually deposited on mold in polymer industry. To be representative of the technological conditions, we have chosen commercial polymers and we propose to study these interactions taking into account the temperature. For this, we have determined, as a function of the temperature, the surface free energy of four nitride based coatings and a DLC coating, the surface free energy of three polymer melts and the wettability of the polymer melt on the different coatings.