Applied Surface Science 371 (2016) 365–375

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Analysis of the low-pressure plasma pretreated polymer surface in terms of acid–base approach

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ARTICLE INFO

*Article history:*
Received 3 November 2015
Received in revised form 18 January 2016
Accepted 29 February 2016
Available online 2 March 2016

*Keywords:*
Acid–base method
Adhesion
Adhesive bonding
Low-pressure plasma
Surface modification

ABSTRACT

We demonstrate the use of a modern wetting method for determining the acid–base properties of treated polymer surfaces for different plastics and adhesives. The effect of the surface treatment with low pressure plasma was evaluated from the viewpoint of acid–base approach with plastics polyoxymethylene (POM) and polyetheretherketone (PEEK). The correlations between the acid–base properties and the identified mechanical tensile strengths of adhesive bonded joints were evaluated and discussed. In the investigated range the determination coefficients for POM and PEEK were calculated to $R^2 = 0.93$ and $R^2 = 0.97$, respectively. These relatively high determination coefficients showed a good correlation between the mechanical strength and the acidity parameter $\Delta D_{short}$ for use in bonding technology for surface pretreatment of polymers with LPP.

## 1. Introduction

Polyetheretherketone (PEEK) is a semi-crystalline thermoplastic material with a high molecular weight, which is characterized by high thermal and chemical stability, high strength, stiffness, toughness and fatigue properties. Due to these properties, PEEK is used in a wide range of applications in automotive, aerospace, chemical and electronics processing industries [1].

The Polyacetal (POM) can be characterized as a semi-crystalline thermoplastic with relative high strength and hardness with a unique balance of mechanical, thermal, chemical, and electrical properties [2]. Another characteristic of POM is also its good tribological resistance. Because of these properties POM is often applied as the material for mechanical, electronic and slide parts.

The selection of a joining technology which is depending on the specific material properties is a prerequisite for their optimum technical application. Regarding this, the adhesive bonding technology has been of great interest in the joining technologies and is widely used. In the field of electronics, PEEK and POM represent very interesting engineering materials [1,3,4]. These materials show processing flexibility associated with many advantages such as chemical stability or excellent thermal and mechanical behavior. Adhesive bonding of this material is a useful technique, but an effective pretreatment procedure is necessary to produce strong bonds.

Surface treatment of polymers by low pressure plasma (LPP) techniques is one of the possible methods for improving the adhesion without changing the bulk properties. Diverse physical, chemical and photochemical effects occurre during the LPP treatment [5,6]. The major effects generated by LPP on polymeric substrates are cleaning, surface activation, etching and crosslinking [7]. Several studies have been performed on the effect of these different plasmas on various polymers in terms of wettability, adhesion improvement, and plasma-induced chemistry at the polymer surface [3,8].

Adhesion ability of polymeric materials is often characterized by surface wetting with different test liquids. However, wetting of the substrate with adhesive, adhesion and mechanical properties of the resulting bonding are fundamentally very complex phenomena. The obtained mechanical properties between the polymeric substrate and the adhesive or paint can be controlled and optimized by varying the adherent formulation, various technological factors as well as the pretreatment of the substrate surface. These

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http://dx.doi.org/10.1016/j.apsusc.2016.02.247
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approaches often have an applied character and do not provide general scientific solutions even for positive technical results.

In the application of solvent-free adhesives acid–base interactions play the major role in the formation of interfacial bonds between adhesives and plastics [9,10]. According to this theory, the best interphase interactions are achieved, when one of the joining partners has a predominantly acidic and the other predominantly basic properties (according to Lewis). Therefore, the knowledge of acidic and basic properties of polymeric materials and adhesives for bonding high performance plastic products is crucial. Since the substrate modification with physical pretreatment methods is a common applied process in the plastics industry, the selection of the necessary modification may also be carried out from the viewpoint of acid–base approach. However, the determination of acidic and basic properties of the treated polymeric surfaces as well as various low molecular weight additives such as fillers, plasticizers etc., is not a trivial task.

### *1.1. Theory*

The traditional and widely used method for the determination of the surface free energy (SFE) and its disperse and polar components is a graphical method based on Owens–Wendt Eq. (1) [11]:

$$W_a = \gamma_L \left(1 + \cos\theta\right) = W^d + W^{AB} = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^{AB} \gamma_L^{AB}}\right) \quad (1)$$

where $W_a$, $W_d$ and $W^{AB}$ represent the thermodynamic work of adhesion and its dispersive and polar part, respectively, $\gamma_L$ and $\gamma_S$ correspond to the SFE of the measurement liquid and solid, respectively, with superscripts d and AB indicating dispersive and polar part of the SFE.

In order to determine the polymer SFE minimum two test fluids with known values $\gamma_L$ are used, which are placed on its surface. After determination of the contact angle, the SFE values are calculated using linear approximation in the coordinates $\sqrt{\gamma_L^{AB}/\gamma_L^d}$ and $W_a/2\sqrt{\gamma_L^d}$. $W_a$ represents the thermodynamic work of wetting with the test fluid. The intercept of the straight line with the ordinate describes the disperse $\left(\sqrt{\gamma_S^d}\right)$ and the straight slope the polar component $\left(\sqrt{\gamma_S^{AB}}\right)$ of SFE. The resulting sum of these values represents the geometric mean of the approximated material SFE $\gamma$.

Using the described graphical method for determination of the SFE components provides very reliable and reproducible results. However, in many empirical studies, it has been observed that the knowledge of the SFE or the polar component is not enough to predict the functionality of polymers [12–15].

The value SFE $\gamma$ does not contain important information about the adhesion ability of the material, since it is predominantly determined by the acid–base component $\gamma^{AB}$ of the SFE. The most important problem achieving high adhesion ability is the reliable determination of the acid–base properties for interacting substrates and adhesives.

Some scientific researchers call this method using the geometric mean to calculate the acid–base components of the SFE into question. However, many research organizations and institutions today use this method, in particular to determine the wetting of solids with liquids to describe the resultant adhesion or adhesion ability. This is often due to the relative simplicity of the process and that the determination of interfacial interaction with other solid-phase methods is practically not possible [12,16].

In 1991 E.J. Berger proposed an extension of the described original graphical method. According to Berger's method the surface properties of polymeric materials are determined using seven different test liquids, two of which have acidic and two basic characters [17]. Another three liquids can be chosen randomly. With this method, the determined values $\gamma_S^{AB}$ are calculated from individual interactions of the two acids and two bases with the surface. The used acids and bases have very similar values of $\gamma_L^{AB}$ and $\gamma_L^d$ (e.g. aniline, formamide, glycerol and phenol). The measured values $\gamma_S^{AB}$ of aniline, formamide, glycerol and phenol at same surface are not identical. The $\gamma_S^{AB}$ differences for acids and bases are used according to Formula (2) to calculate parameter D (also called acidity parameter) which describes the acid–base-properties of the surface.

**Table 1**
Parameters for test liquids [20].

| Test liquid | $\gamma_L$ [mN/m] | $\gamma_L^{LW}$ [mN/m] | $\gamma_L^{AB}$ [mN/m] |
|---|---|---|---|
| Water | 72.0 | 22.0 | 50.0 |
| Ethylene glycol | 48.3 | 29.3 | 19.0 |
| Diiodomethane | 50.8 | 50.8 | 0.0 |
| Aniline | 43.2 | 41.2 | 2.0 |
| Phenol | 40.4 | 37.8 | 2.6 |
| Formamide | 58.3 | 32.3 | 26.0 |
| Glycerol | 64.0 | 34.0 | 30.0 |

$$D = 2\left[\sqrt{\gamma_S^{AB}(aniline)} + \sqrt{\gamma_S^{AB}(formamide)}\right] - 2\left[\sqrt{\gamma_S^{AB}(phenol)} + \sqrt{\gamma_S^{AB}(glycerol)}\right] \quad (2)$$

A value of D > 0 corresponds to acidic and D < 0 to basic character of the surface. A possible application of the parameter D to determine the acidity of the surface has been repeatedly demonstrated in practice [18,19]. In recent years the parameter D has proven to deliver quite reliable measurements for modified and unmodified polyethylene, rubber and various epoxies as well as metal substrates. In these studies, a lot of surfaces of different nature were analyzed and the results show that the Berger method is a correct and chemically reasonable method of surface characterisation [10,18].

The theoretical limit of any wetting method is the spreading of a test liquid on the substrate surface, because in this thermo dynamical state the contact angle cannot be determined. If we consider the SFE values of various testing liquids (Table 1), we can see that the limit of the presented Berger method is represented by phenol with $\gamma_L = 40.4$ mN/m and aniline with $\gamma_L = 43.2$ mN/m. The polar component for these test liquids are $\gamma_L^{AB} = 2.6$ and $\gamma_L^{AB} = 2.0$ mN/m, respectively.

For a correct surface energy calculation with values $\gamma_S \geq 40.4$ mN/m a shortened version of the Berger method was introduced. In the shortened version from equation (2) one acid and one base with the corresponding lower values of SFE have been removed. Thus, the difference in values between $\gamma_S^{AB}$ of formamide and glycerol can now be calculated by Formula (3). The result is a measurement of surface acidity or basicity and is called a short acidity parameter or parameter $D_{short}$.

$$D_{short} = \left[\sqrt{\gamma_S^{AB}(\text{formamide})}\right] - \left[\sqrt{\gamma_S^{AB}(\text{glycerol})}\right] \quad (3)$$

To evaluate the substrate adhesion ability regarding the acid–base properties of the adhesive within the present work the quantity $\Delta D_{short}$ was introduced, which is calculated as indicated in Eq. (4).

$$\Delta D_{short} = \left|D_{short}^{adhesive} - D_{short}^{substrate}\right| \quad (4)$$

Increasing the value of $\Delta D_{short}$ shows increased functionality of adhesive and substrate and thus corresponds to an increase