

Research Article

Characterization of Polymer Surfaces by the Use of Different Wetting Theories Regarding Acid-Base Properties

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The existing wetting methods for the determination of acid-base properties on solid surfaces are discussed. Striving for a better understanding of the adhesive polymer interactions in adhesively joined polymers, the methods of Berger and van Oss-Chaudhury-Good were found as the most suitable methods for the investigation of wetting on solid polymer surfaces. Methods of nonlinear systems by Della Volpe and Siboni were adapted and evaluated on plastic surfaces. In the context of these investigations various data of the surface free energy as well as its components have been identified for a number of polymer surfaces by application of spatial equation solutions.

1. Introduction

Polymers are often characterized by their wetting behavior with respect to adhesion. The resulting adhesion between the polymeric substrate and the adhesive can be impinged and optimized by the variation of the adhesive formulation, various technological factors, and surface treatment of the substrate. However, these factors are in application-oriented nature and provide no generally accepted scientific solutions, even for positive technical results.

It is well known that wetting and the resulting adhesion represent very complex phenomena. However, it is also proven that in most cases the acid-base interactions play the main role in the formation of interfacial forces by adhesive bonding between adhesives and plastics [1]. The best interfacial interactions can thereby be obtained if one of the materials has primarily acidic and the other one basic properties (according to Lewis). In this respect, the knowledge of the acidic and basic surface properties is of crucial importance for the polymeric materials and the adhesives by the creation of high strength polymer-polymer and polymer-metal adhesive joints. However, since the modification of the adhesive and the substrate for the formation of the boundary

surface in the polymeric adhesive compound is an important process, the proper selection of the necessary modifications can be adapted from the viewpoint of the acid-base approach. The determination of the acidic and basic properties of the resulting “finished” polymer surfaces as well as of various low molecular weight additives such as fillers and plasticizers is not a trivial task. The study and analysis of existing methods tested in this paper allow the evaluation of acidic and basic properties of polymers and polymer adhesive joints.

1.1. Theoretical Aspects of the Acid-Base Approach. The acid-base properties of materials are determined by the surface free energy (SFE), which according to Fowkes consists of several additive components [2]

$$\gamma = \gamma^d + \gamma^i + \gamma^p + \gamma^h + \gamma^\pi + \gamma^{ad} + \gamma^e. \quad (1)$$

Here, the subscript d relates to the dispersion interaction and *i* refers to inductive dipole-dipole, p- to dipole-dipole, h- to hydrogen and π - to π -bonds or interactions by formation of π -complexes, e- to electrostatic, and ad to donor-acceptor interaction. The combinations in which bonds between an electron acceptor (such as cation, metal, or metal salt) and

an electron donor (e.g., unsaturated or aromatic bond) are formed by integration with a π -electron to a donor group are grouped in a π -bond at the same time.

According to Van Oss et al. [3, 4] the first three terms in (1) may be combined in a single Lifshitz-van-der-Waals component

$$\gamma^{LW} = \gamma^d + \gamma^i + \gamma^p. \quad (2)$$

It should be noted that the energies of induction γ^i and dipole-dipole interactions γ^p are represented as ones of the second order of magnitude compared to the dispersion interaction. Fowkes and Mostafa combined the last four terms γ^h , γ^π , γ^{ad} , and γ^e of (1) in an acid-base component γ^{AB} [5]

$$\gamma^{AB} = \gamma^h + \gamma^\pi + \gamma^{ad} + \gamma^e. \quad (3)$$

Thereby, in most cases the surface free energy can be determined by the addition of the Lifshitz-van der Waals and the acid-base component.

$$\gamma = \gamma^{LW} + \gamma^{AB}. \quad (4)$$

Mathematical notation of the first component has been proposed as a combination rule of Good and Girifalco [6].

The magnitude of the entire surface free energy γ contains no significant information about the interacting capability of the material. The potential for adhesive interaction is defined by the acidic and basic properties (i.e., γ^{AB}) of the surface. Therefore, the first task is the reliable determination of acid-base properties for relevant adhesives and adherents with the aim of achieving high adhesion. Some promising methods for the determination of these parameters are discussed below.

1.2. Methods for the Determination of Acidic and Basic Properties of Materials. The current methods for determining the acid-base properties of various materials as well as for further analysis show different quantitative characteristics. However, as the performed comparative analysis shows, not all of these methods have a universal applicability and some only provide limited information.

For example, the methods of Drago [7] and Gutmann [8] can provide only one value of the acidity or basicity. The amphoteric properties of substances are absolutely neglected in their methods [7, 8].

The major disadvantage of these and many other modern studies of the acid-base interactions is that the researchers usually apply for acid or base models only and ignore the fact that almost every substance may have a certain bipolarity. All plastics up to polymers with macromolecular chains of saturated hydrocarbons possess both acidic and basic properties. Thus, for example, polyethylene terephthalate (PET) according to general assumptions is a base and polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) are acids. However, according to in-depth analysis and calculations of the acidic and basic parameters, the assumption that the polymer surfaces are monopolar is incomplete or incorrect [9].

A wetting process of the surface with solutions of acids and bases as test liquids may only be used for the neutral

and hydrophobic surfaces using liquids with a relatively high surface free energy of the solvent. For the determination of adsorption isotherms of test-acids or bases, the equation of Gibbs adsorption by using an adsorption isotherm can be used. This way the concentration of acidic and basic centers on the surface can be calculated and plotted. This method can be used to determine the Drago constants and the chemical nature of the modifier used to improve wetting and adhesion of the polymer [10].

A traditional and common method for determining the disperse and polar (acid-base) components of the surface free energy is a graphical method, which is based on the equation by Owens-Wendt (5) [11].

$$\begin{aligned} W_a &= \gamma_L (1 + \cos \theta) = W^{LW} + W^{AB} \\ &= 2 \left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^{AB} \gamma_L^{AB}} \right). \end{aligned} \quad (5)$$

Based on this equation, the contact angle measurements on the surface and the known values γ_L of the test liquids are applied in the linear approximation in coordinates $\sqrt{\gamma_L^{AB}/\gamma_L^{LW}}$ versus $W_a/2\sqrt{\gamma_L^{LW}}$ (where W_a represents the thermodynamic work of adhesion with the test liquids). The intersection of the curve with the ordinate describes the disperse component $\sqrt{\gamma_S^{LW}}$, while the slope of the straight line describes the polar component $\sqrt{\gamma_S^{AB}}$. The resulting sum of both components represents the geometric mean of the approximated total surface free energy of a solid material.

Application of this graphical method for determining the components of the surface free energy provides very reliable and reproducible results. However, in many empirical studies it was very often ascertained that only the knowledge of the acid-base component is not entirely sufficient to predict the functionality of a polymer or a plastic [12].

In 1991 Berger suggested an amendment or extension of this graphical method. In the Berger method the surface acidity of polymeric and metallic materials is determined by seven different test liquids, two of them bear an acidic and two a basic character (according to Lewis) [13]. First, the values γ_S^{AB} from the individual interactions with two acids and two bases are determined. The acids-base pairs used here have very similar values of γ_L^{AB} and γ_L^{LW} (phenol, aniline, glycerol, and formamide). If there were no acid-base interactions between the substrate and the corresponding test liquid, the same contact angles and values γ_S^{AB} for aniline, phenol, glycerol, and formamide could be measured. But this does not correspond to reality. The difference in the measured contact angles resulting in different values γ_S^{AB} of the acid and base pairs, which can be calculated by formula (6), represents a way to measure the acidity or basicity of the surface and is referred to as the acidity parameter D .

$$\begin{aligned} D &= 2 \left[\sqrt{\gamma_S^{AB}(\text{Aniline})} + \sqrt{\gamma_S^{AB}(\text{Formamide})} \right] \\ &\quad - 2 \left[\sqrt{\gamma_S^{AB}(\text{Phenol})} + \sqrt{\gamma_S^{AB}(\text{Glycerine})} \right]. \end{aligned} \quad (6)$$

The value $D > 0$ corresponds to an overall acidic character and $D < 0$ to a basic character of the surface.

The last two methods which use the geometric mean for calculating acid-base components of the surface free energy in their calculations are called into question by some researchers. However, today many research institutions use exactly these methods to determine the wetting of solids with a liquid to take a statement on the resulting adhesion. This is due to the relative simplicity of the procedure and by the fact that the determination of interfacial interaction with a solid phase is almost impossible with other methods. However, the possible use of the parameter D has already been demonstrated in practical applications. In particular, the parameter D has been established in recent years for modified and unmodified polyethylene, rubber, and epoxy coatings of various metal substrates [14]. So, many surfaces of different natures have been analyzed and it has been proved that the Berger method is a correct and chemically reasonable method for surface characterization. For an application of the procedure in adhesive joining technology many plastics have been studied in this work.

2. Experimental

2.1. Materials. The thermoplastics were processed from granules to plates with dimensions of $50 \times 150 \times 3$ mm on an injection molding machine TM 1300/525 + 130L UNILOG B4 (Wittman Battenfeld GmbH & Co. KG, Meinerzhagen, Germany). The roughness characteristics of the injection mold surface were $R_a = 0.11 \pm 0.01 \mu\text{m}$, $R_q = 0.13 \pm 0.01 \mu\text{m}$, and $R_z = 0.38 \pm 0.10 \mu\text{m}$. Processing parameters such as drying time and temperature (if necessary), injection pressure, cylinder temperature, holding pressure, and cooling time were selected strictly according to the recommendations of the material manufacturers from the data sheets. PTFE and PVC-U were available for the tests as plates with dimensions $50 \times 150 \times 3$ mm. The adhesives used were measured in cured state (curing was done according to the recommendations of the adhesive manufacturers) with the method of sessile drop. For this purpose, the adhesive samples were applied on a PTFE plate in a liquid state and cured at standard conditions (23°C ., 50% relative humidity).

2.2. Methods. The performed SFE measurements were carried out using the method of the sessile droplet on solid surfaces in accordance with DIN 55660-2. A drop shape analyzer DSA 30 (Krüss Optronic GmbH, Hamburg, Germany) was used to measure the contact angle. The test liquids used were diiodomethane, ethylene glycol, formamide, glycerol, aniline, 88% phenol solution, and deionized water (all p.a. purity). At least five droplets were deposited for each liquid. The angle setting of the CMOS camera was set to the recommended angle of 2° and the magnification factor to 200 pixels/mm. In the case of the test liquids diiodomethane, ethylene glycol, and water, the contact angle was measured immediately after the droplets were deposited on the solid surface. For the formamide, glycerol, aniline, and 88% phenol solution, the contact angle was determined after the thermodynamic stability had been reached (after 2 minutes). This approach

has been proposed in [15]. All measurements were carried out at standard 23/50 conditions.

3. Results

The measured values of the surface free energy components and the corresponding parameter D are summarized in Table 1.

Unlike γ_s^{AB} the acidity parameter D provides direct information of acid-base properties of the surface. Thus, the surface of polycarbonate (PC) with $D = -1.15$ (mN/m) $^{1/2}$ has a dominantly basic character conditioned by the presence of oxygen atoms in the main chain and strong nucleophilicity of the carbonyl oxygen atoms. The polyvinylchloride (PVC-U) with $D = 1.30$ (mN/m) $^{1/2}$ has acidic properties. This example can also explain the influence of surface preparation on the acid-base properties of the surface (e.g., time, pressing temperature) and allows the integral characterization of solid substrate surfaces.

The acid-base component of each phase can be written as $\gamma_i^{\text{AB}} = 2\sqrt{\gamma_i^+ \gamma_i^-}$ and the total work of adhesion can be expressed in the following form:

$$\begin{aligned} W_{\text{LS}} &= -\Delta G_{\text{LS}} = (1 + \cos \theta) \gamma_{\text{L}} \\ &= 2 \left(\sqrt{\gamma_{\text{L}}^{\text{LW}} \gamma_{\text{S}}^{\text{LW}}} + \sqrt{\gamma_{\text{L}}^+ \gamma_{\text{S}}^-} + \sqrt{\gamma_{\text{L}}^- \gamma_{\text{S}}^+} \right). \end{aligned} \quad (7)$$

From a practical point of view, (7) creates the possibility of calculating the dispersion and the electron donor and electron acceptor components of the surface free energy for a solid body having at least three test liquids. However, the difficult problem that needs to be solved is the determination of γ^- and γ^+ components of the different test liquids. One of the test liquids is usually water. According to van Oss the ultrapure water has acidic and basic properties in equal measure at 20°C . He therefore proposed water $\gamma_{\text{L}}^- = \gamma_{\text{L}}^+ = \gamma_{\text{L}}^{\text{AB}}/2 = 25.5$ mN/m. However, using this method, he has found that the obtained results are strongly depending on the choice of the test liquid. In addition, as defined by van Oss the acid (γ^+) and base- (γ^-) parameters were not ideally determined for the test liquids. Their use in the calculation of the SFE therefore resulted in reduced values of the electron acceptor parameters for a number of polymers. As a result, most polymer surfaces were defined as basic, what was known in the scientific literature as “basic disaster” [16]. Despite these shortcomings, the van Oss-Chaudhury-Good (VCG) theory has the most followers and the method itself is one of the basic and popular methods used to determine the surface free energy of polymers.

As a part of this work, the method VCG was tested. The main purpose of this study was the correct definition of acidic and basic parameters of different test liquids. For this purpose a modification of the method VCG by Della Volpe and Siboni (DVS) has been proposed [17–19]. The resolution of a system of nonlinear equations (8) was possible:

$$\begin{aligned} \gamma_{\text{L},i} &= \gamma_{\text{L},i}^{\text{LW}} + 2\sqrt{\gamma_{\text{L},i}^+ \gamma_{\text{L},i}^-}, \quad \forall i = 1 \cdots L, \\ \gamma_{\text{S},j} &= \gamma_{\text{S},j}^{\text{LW}} + 2\sqrt{\gamma_{\text{S},j}^+ \gamma_{\text{S},j}^-}, \quad \forall j = 1 \cdots S, \end{aligned}$$

TABLE 1: Surface free energy components and acidity parameter D for different nonmodified polymers.

Substrate	γ_s^{LW} [mN/m]	γ_s^{AB} [mN/m]	D [(mN/m) ^{1/2}]
2C-Epoxy adhesive	40.23	7.77	2.25
2C-MMA adhesive	27.95	5.41	4.33
2C-PUR adhesive	31.13	6.85	3.36
Polycarbonate (PC)	38.07	0.45	-1.75
Polyethylene terephthalate (PET)	33.29	3.33	-0.85
Polymethylmethacrylate (PMMA)	39.7	3.0	0.95
Polypropylene (PP)	33.52	0.87	0.55
Polystyrene (PS)	39.69	0.04	-1.80
Polytetrafluoroethylene (PTFE)	24.30	0.06	0.00
Polyvinyl chloride, unplasticised (PVC-U)	37.70	0.80	1.30

TABLE 2: Surface free energy, its components, and parameters for the test liquids, which were calculated by the simplified nonlinear system.

Test liquid	γ_L [mN/m]	γ_L^{LW} [mN/m]	γ_L^+ [mN/m]	γ_L^- [mN/m]	γ_L^{AB} [mN/m]
α -bromonaphthalene	44.6	44.6	0.0	3.0	0.0
Aniline	43.2	41.2	0.2	5.7	2.0
Diiodomethane	50.8	50.8	0.0	1.3	0.0
Dimethylformamide	37.3	32.4	2.4	2.5	4.9
Dimethyl sulfoxide	43.6	34.9	2.1	9.1	8.7
Ethylene glycol	48.3	29.3	12.1	7.5	19.0
Formamide	58.3	32.3	5.2	32.4	26.0
Glycerol	64.0	34.0	32.7	6.8	30.0
Phenol (water solution)	40.4	37.8	6.4	0.3	2.6
Water	72.0	22.0	28.3	22.2	50.0

$$\begin{aligned} & \gamma_{L,i} (1 + \cos \theta_{i,j}) \\ &= 2 \left(\sqrt{\gamma_{L,i}^{LW} \gamma_{S,j}^{LW}} + \sqrt{\gamma_{L,i}^+ \gamma_{S,j}^-} + \sqrt{\gamma_{L,i}^- \gamma_{S,j}^+} \right). \end{aligned} \quad (8)$$

Here the indices L and S correspond to the indices of liquids and solids, respectively. The values of the surface free energy ($\gamma_{L,i}$) are taken from literature and the wetting angle θ_{ij} was determined experimentally. The advantages of this system are characterized by absolute freedom of surface free energy components with the exception of the total surface free energy of the test liquids.

The system was set up for six liquids and four solid surfaces. In this case, the minimum number of nonlinear equations to be solved is 34 ($6 + 4 + 6 \times 4$). In the calculation of solutions for some substances the result was far from the real values. Such systems are usually solved using the method for multidimensional optimization. However, this offers no solution in the case of large nonlinear equations.

Therefore, a simplification of the system was carried out by reducing the number of unknowns and the use of Lifshitz-van der Waals components γ^{LW} of the surface free energy for liquids and solid surfaces. Consequently, the first version of

the simplification of (8) to the solution of equations is reduced to four of the following types:

$$\begin{aligned} & \left(\frac{\gamma_{L,i} (1 + \cos \theta_{i,j})}{2} - \sqrt{\gamma_{L,i}^{LW} \cdot \gamma_{S,j}^{LW}} \right)^2 \\ & - \frac{(\gamma_{L,i} - \gamma_{L,i}^{LW})(\gamma_{S,j} - \gamma_{S,j}^{LW})}{2} \\ & = \gamma_{L,i}^+ \cdot \frac{\gamma_{S,j} - \gamma_{S,j}^{LW}}{4\gamma_{S,j}^+} + \gamma_{S,j}^+ \cdot \frac{\gamma_{L,i} - \gamma_{L,i}^{LW}}{4\gamma_{L,i}^+}. \end{aligned} \quad (9)$$

As a result, the solution of these simultaneous equations (9) was obtained by surface free energy parameters of the test fluids, which are shown in Table 2.

These parameters are generally slightly different from those that are provided by scientific literature at this point. For aniline and 88% aqueous solution of phenol, parameters appear for the first time. Thus, aniline, formamide and dimethylformamide have a basic, glycerol, ethylene glycol, and aqueous solution of phenol an acidic character. The scientific view that water predominantly has acidic properties (due to the absorption of CO₂ from the air) can be confirmed by these measurements. According to the collected

TABLE 3: Surface energy, its components, and parameters for certain polymers.

Material	γ_s^{LW} [mN/m]	γ_s^+ [mN/m]	γ_s^- [mN/m]	γ_s^{AB} [mN/m]	γ_s [mN/m]	D [(mN/m) ^{1/2}]
2C-Epoxy adhesive	40.23	5.97	1.16	7.77	48.0	2.25
2C-MMA adhesive	27.95	6.25	0.01	5.41	33.36	4.33
2C-PUR adhesive	31.13	5.25	0.30	6.85	37.98	3.63
Polycarbonate (PC)	38.07	0.13	0.40	0.45	38.52	-1.75
Polyethylene terephthalate (PET)	33.29	1.59	1.74	3.33	36.62	-0.85
Polymethylmethacrylate (PMMA)	37.7	2.1	1.2	3.2	40.9	0.95
Polypropylene (PP)	33.52	0.48	0.40	0.87	34.39	0.55
Polystyrene (PS)	39.69	0.00	0.14	0.04	39.73	-1.80
Polytetrafluoroethylene (PTFE)	24.30	0.01	0.10	0.06	24.36	0.00
Polyvinyl chloride, unplasticised (PVC-U)	37.70	0.90	0.18	0.80	38.50	1.30

data and to the latest data from literature the liquids α -bromonaphthalene and diiodomethane are not completely dispersive liquids [4, 20].

The proposed nonlinear method is relatively complex in the mathematical construction. Applied to the determination of the surface free energy parameters of polymers, there are several possible solutions. Its use is therefore very limited due to the wide possible choice of the best solution.

The challenge has been to get a unique solution for the surface free energy parameters of solid surfaces by modification of vOCG equation for equation of the form $z = Ax + By + C$:

$$\frac{\gamma_L (1 + \cos \theta)}{2\sqrt{\gamma_L^-}} = \frac{\sqrt{\gamma_L^{LW}}}{\sqrt{\gamma_L^-}} \cdot \sqrt{\gamma_s^{LW}} + \frac{\sqrt{\gamma_L^+}}{\sqrt{\gamma_L^-}} \cdot \sqrt{\gamma_s^-} + \sqrt{\gamma_s^+}. \quad (10)$$

With the known values of the parameters of test liquids and the cosine of the contact angle of test liquids, a plane in coordinates $(\sqrt{\gamma_L^{LW}}/\sqrt{\gamma_L^-}; \sqrt{\gamma_L^+}/\sqrt{\gamma_L^-}; \gamma_L(1 + \cos \theta)/2\sqrt{\gamma_L^-})$ was constructed with multivariate approximation.

The calculation of the coefficients A, B, and C was then carried out in the program "Statistica." The coefficient A is equal to the square root of the Lifshitz-van der Waals component of the solid surface $(\gamma_s^{LW})^{1/2}$, the factor B is the root of the basicity parameter $(\gamma_s^-)^{1/2}$, and the coefficient C is equal to the root of the acidic parameter $(\gamma_s^+)^{1/2}$. Figure 1 shows the spatial calculation for a generic PMMA surface.

About fifty different surfaces were characterized by the method described including polymers, metal substrates, and glass surfaces. Table 3 shows the components and parameters of the surface free energy for some examined plastics.

The reliability of the obtained results was confirmed by a quantum-chemical analysis of the investigated substrates with Bader density functional theory [21–23] and by the Berger method. Therefore, it can be said that the determination of acidic and basic properties of solid surfaces by means of spatial methods can provide meaningful information in accordance with the energetic structure and composition of the investigated objects.

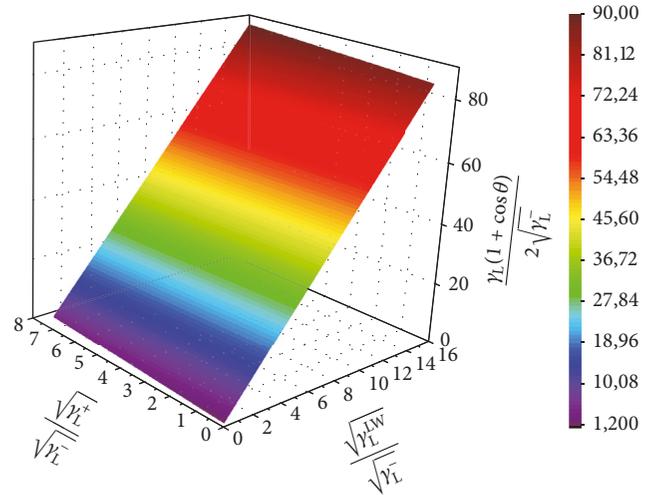


FIGURE 1: Definition of γ_s^{LW} , γ_s^+ , and γ_s^- for PMMA with spatial method.

4. Resume

The analysis of the existing methods for the determination of acidic and basic properties of solid surfaces led to the following results.

From the variety of methods no "ideal" method, which offers a flawless solution for every application, could be singled out. However for solving specific practical problems, some of the methods seem to be more accessible and more informative. From the above-mentioned methods, organic and inorganic methods for the assessment of the wetting angle and especially the methods of Berger and van Oss-Chaudhury-Good with modification according to DVS and solutions in spatial dimensions for determining the surface properties can be highlighted.

The Berger method creates the possibility of controlling both the influence of the modification of polymeric materials and processing methods for the formation of various coatings. Parameter D reflects the chemical nature of the surface and provides useful information, for example, for the design of the adhesive systems with the desired properties.

The theory VCG is definitely a good tool for the determination of acidic and basic properties of polymer surfaces. It is also practical for establishing an assessment of energy of the interfacial interactions with the ability of defining energy surface modification as well as the surface design. This method is consistent with modern scientific ideas of the physical chemistry of surface phenomena. In its practical application, however, this procedure is associated with some difficulties presented.

The modified method DVS is a promising approach for the process according to VCG, since in this case the number of “questionable” constants is minimized. However, the complexity of the mathematical design leads to strong dependence of the calculated values on experimental errors.

For a scientifically based selection of test liquids, the following aspects should be considered. Since the acid-base parameters for solids to be determined are defined by the liquid parameters and contact angles, the choice of test liquids plays a decisive role. In order to obtain the best possible results, the absolute distances between the plane defining points, resulting from liquid parameters, should be as far as possible from each other. The parameter of chosen liquids should not lie on a straight line. This reduces the incidence of errors. Other aspects of the test liquid selection include for example, avoidance of surface solvent effects, viscosity, and aging of the test liquid.

The particular interest of the presented methodology is the application in adhesive joining technology. Currently, the German Plastics Center (SKZ) in cooperation with Kazan National Research Technological University (KNRTU) is examining the correlations between the determined parameters of the SFE for adhesions and adherents and the resulting mechanical short-time properties for plastics and various adhesives with this method. Subsequently, the described method should be validated and implemented in various analytical solutions.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

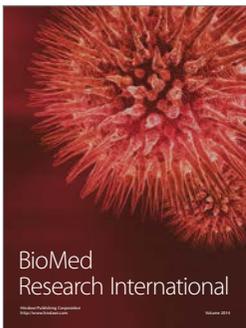
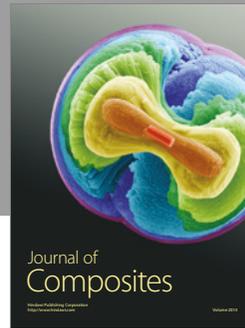
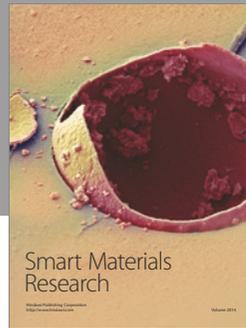
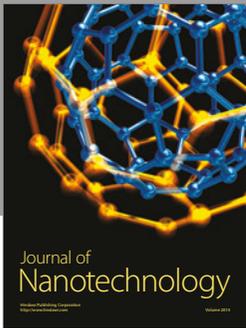
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