

CONTACT ANGLE MEASUREMENTS IN STUDY OF POLYMERS
FOR CREATION OF MATERIALS

Yulia G. Bogdanova, Valentina D. Dolzhikova, Alexander Yu. Alentiev, Ilya M. Karzov
Moscow Lomonosov State University,
^{1/3}Leninskie Gory, Moscow 119991, Russia
yulibogd@yandex.ru

Abstract

The possibilities of contact angle measurements of liquids at the solid surfaces under the different conditions for prediction of the most perspective directions of polymer application for individual and composite materials creation are considered. The surface free energy values at the «solid-gas» and «solid-liquid» interfaces as parameters of such prediction are exhibited. The correlation of the dispersive component of polymer surface energy with its free volume is founded. The new approach to estimation and comparison of the intensity of polymer adhesion to inorganic substrates is proposed and experimentally proved by measurements of tensile strength of corresponding composite materials. The possibility of alteration of «polymer-liquid» interfacial energy with surfactant mixed adsorption layers is demonstrated.

Key words: contact angle, wetting, adhesion, blood compatibility, free volume, composite materials, adsorption, surface energy, interfacial energy, surfactant mixtures, Pluronic

1. INTRODUCTION

Polymers are widely used in different aspects of the field of science of materials as adhesives and dresses of fibers in creation of constructional materials of various applications, base for creation of materials for medicine and biology, membrane materials and so on. In present time the main task of design of macromolecules is the development of principals permitted to synthesize polymers with specified physical-chemical properties. But it is necessary to take into account the key role of «polymer-medium» interface in variety of processes on the path of polymer to material and on service of polymer material. So, it is desirable to have some parameters which may be used to predict the polymer behavior in contact with different media. The specific surface free energy of polymers γ_{SV} and «polymer-liquid» interfacial energy γ_{SL} can be such parameters.

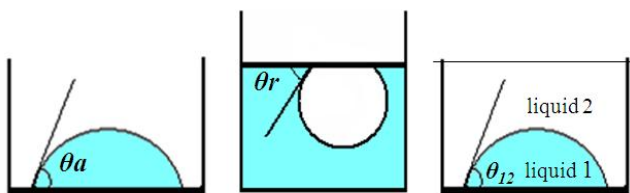


Fig. 1. Scheme of contact angles determination
at the various conditions.

Among a number of methods permitted to determine the γ_{SV} only few ones are appropriate for polymers [1]. The number of methods for γ_{SL} determination is more restricted [1]. The measurements of advancing (θ_a), receding (θ_r) contact angles and contact angle in preferential wetting conditions (θ_{12}) allow to determine γ_{SV} and γ_{SL} (Fig.1). For a long time this method is successfully used in spite of the number still unsolved problems of wetting theory and

difficulties of experimental data interpretation for real systems [2-4].

2. THEORY

The principal possibility of the determination of polymer surface energetic characteristics appears from the Young equation for equilibrium contact angle (θ) of liquid droplet on the solid surface:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

γ_{SV} , γ_{SL} , γ_{LV} are accordingly values of free surface energy of solid/vapor, solid/liquid and liquid/vapor interfaces [2]. In accordance to thermodynamic the solid must be in balance with liquid and one's saturated vapor. Thus, the problem of adsorption of liquid from vapor onto solid surface leads to γ_{SV} decrease due to the film pressure (π) of liquid adsorption layer in front of perimeter of drop takes place if the experimental aim is to determine the γ_{SV} value [5]:

$$\cos \theta = (\gamma_{SV} - \gamma_{SL} - \pi) / \gamma_{LV}.$$

Usually the solid surfaces are divided in high energy (metals, ionic crystals) and low energy ones (particularly it is majority of polymers) [5, 6]. It is the rule to possess that in case of low energy surface the π value is negligibly low in comparison to γ_{SV} , and γ_{SV} is constant during the testing of surface by contact angle. The γ_{SV} value, divided high and low energy surfaces, is rather conditional. For example, according to [6] it must be $\gamma_{SV} \approx 60$ mJ/m². Estimation of water advancing contact angle ($\theta_a^{(w)}$) at such surface at 20°C using Young equation and Antonov's rule [1] gives $\theta_a^{(w)} > 50^\circ$. At the same time in [2] it is pointed that $\gamma_{SV} = \text{const}$ up to $\theta_a^{(w)} > 10^\circ$. Another assumption of $\gamma_{SV} = \text{const}$ is the case when the criterion for test liquid $\gamma_{LV} < \gamma_{SV}$ is fulfilled. Thus, the problem of determination of conditions when π accounting is necessary, is not yet dissolved completely. Nevertheless, the assumption about $\gamma_{SV} = \text{const}$ permits to use contact angle measurements as the method for γ_{SV} value of polymers determination [2, 7, 8].

Also it should be taken into account that Young equation is valid to ideally smooth solids with homogeneous surfaces which do not interact with test liquids by chemical bonds formation, dissolution or swelling. Practically the infinite set of metastable states can be realized during the wetting of solid surface with test liquid [3, 5]. So, the static contact angles are not necessary the equilibrium contact angles. That is why it is important to standardize carefully the choice of experimental samples of each polymer using measuring of the advancing and receding contact angles of liquid (usually it is distilled water) preliminary to the γ_{SV} and γ_{SL} determination.

The theoretical approaches to γ_{SV} determination using contact angle measurements can be divided on two groups. One of them bases on molecular theory of wetting, others use thermodynamic equation of state for interfacial tension of solid – liquid systems [2, 5]. The main advantage of molecular theory of wetting is the possibility to determine the components of the γ_{SV} value which, in general, are the mirrors of non-compensate attractive polar and dispersive intermolecular interactions inside the solid phase.

So, this possibility permits to understand how these interactions must be changed, for example, using inclusion of substituent in monomer link, to provide the desirable surface property of polymer. In turn, this fact makes the contact angle measurements very informative and relatively express method for physical-chemical analysis of new polymers and comparison of properties of numbers of related polymers with different side groups.

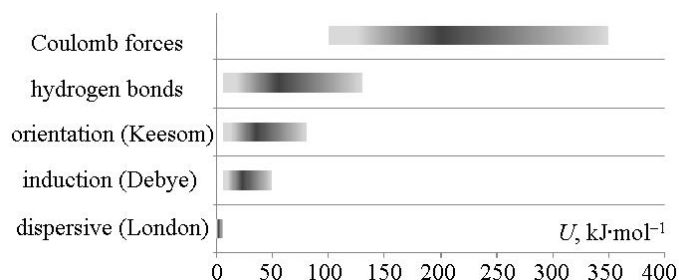


Fig.2. The relation of energies of non covalence interactions [9].

dispersion forces and γ_{SV}^{ab} represents acid-base interactions which realized by donor-acceptor mechanism between the Lewis acids or bases and dominate over all polar interactions (in particular, Keesom and Debye forces) inside solid phase.

But it should be pointed that the contribution of each component in total γ_{SV} still not determined exactly. So, the problem of determination of γ_{LV} components also exists for test liquids. For all these liquids the corresponding components of surface tension γ_{LV} must be known. It should be mentioned that values of γ_{LV}^d , γ_{LV}^p and γ_{LV}^{LW} for the test liquids obtained at the different works are in a good agreement [4, 7]. At the same time the γ_{LV}^{ab} values (namely, γ_{LV}^+ and γ_{LV}^-) differ for the same liquid [8]. This fact must be taken into account in choice of test liquids and methods for the determination of γ_{SV} and its components.

In spite of dispersion forces provide minimal attractive energy in comparison to other intermolecular attractive forces (Fig. 2), the additivity of dispersion interactions makes it considerably more long-range in comparison to orientation and induction ones. So, namely dispersive interactions will possess by the special sensitivity to package density of polymer chains in surface layer which indicates the package density inside the polymer phase. Thus, the surface energy characteristics, certainly γ_{SV}^d , may be informative for prediction of polymer application for membrane materials.

It is not quite sufficient to know only the γ_{SV} and its components to predict the possible ways of polymer application for practice tasks decision. The possible macromolecular mobility in interfacial layer contacting with different media (especially, liquids) may cause changes in pack of polymer chains so as decrease the interfacial energy γ_{SL} . So, even the mechanical stability of polymer material may change in result of its longstanding contact with liquid due to [spontaneous](#) dispersgating of polymer into liquid phase if γ_{SL} value is too low ($\gamma_{SL} < 1 \text{ mJ} \cdot \text{m}^{-2}$) [10]. Thus, the determination of polymer γ_{SL} at the interfaces with liquids of different polarity is necessary. The first works concerning this problem were performed by E. Ruckenstein and coworkers with respect to problem of blood compatibility of polymer materials [10-12]. It was shown that the behavior of polymer material in biological environment is determined by its equilibrium interfacial energies: $\gamma_{S(W)W}$ (polymer-water), γ_{SO} (polymer-octane) and $\gamma_{S(O)W}$ (polymer, saturated octane-water). So, the special technique permitting to determine mentioned values was developed [11, 12]. This technique includes the measurements of contact angles of water droplet θ_W and air bubble θ_V at the polymer surface after contact with octane during 24h and the measurement of contact angle of water droplet at the polymer surface contacting with octane θ_{OW} during 24h (Fig. 3). Equations permitting to calculate $\gamma_{S(W)W}$, γ_{SO} and $\gamma_{S(O)W}$ using θ_W , θ_V and θ_{OW} experimental values are presented in [11,12].

Many different approaches for determination of γ_{SV} and its components using molecular wetting theory are developed [2, 5]. The main difference between these approaches is the attempt to divide γ_{SV} to the components:

1) $\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p$, where γ_{SV}^d includes London interactions and γ_{SV}^p includes Keesom, Debye forces and hydrogen bonds;

2) $\gamma_{SV} = \gamma_{SV}^{LW} + \gamma_{SV}^{ab}$, where γ_{SV}^{LW} represents Lifshits-van der Waals

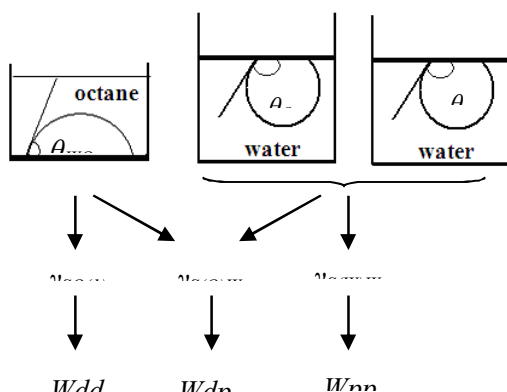


Fig. 3. Scheme of experimental determination of polymer work of adhesion to model liquids. Contact angles are marked in accordance to [12].

and polymerizing inoculating [13, 14]. The advantage of adsorption modifying of polymer surfaces with surfactant adsorption layers is stability of mechanical characteristics of polymer material while surface characteristics changes. But the modifying layers at the polymer surface must be stable.

Water and octane appeared to be very convenient model objects with respect to problem of polymer adhesion to the different substrates. First, it may simulate polar and non polar phases with respect to comparison of adhesive properties of polymers. Second, octane surface tension value $\gamma_{LW} = 21,8 \text{ mJ}\cdot\text{m}^{-2}$ is the same for one for surface tension dispersion component of water [8]. This fact simplifies the equations for calculation of $\gamma_{S(W)W}$, γ_{SO} and $\gamma_{S(O)W}$ [11, 12].

The parameters permitting to predict and to compare the adhesion properties of polymers are the work of adhesion values:

to non polar phases (model liquid is octane) $Wdd = \gamma_{SV} + \gamma_{LV}(\text{octane}) - \gamma_{SO}, \quad (1)$

to polar phases (model liquid is water) $Wpp = \gamma_{SV} + \gamma_{LV}(\text{water}) - \gamma_{S(W)W}, \quad (2)$

to non polar and polar phases both $Wdp = \gamma_{SO} + \gamma_{LV}(\text{water}) - \gamma_{S(O)W}.$

This new approach for prediction of adhesion of polymers to inorganic substrates (in diffusion «polymer-substrate» absence) is presented by us in details in work [15]. In this work the number of advantages of one in comparison to other existing approaches for estimation and comparison of adhesion using contact angle measurements [5, 16, 17]:

- using of equilibrium values of «polymer-model liquid» interfacial energy for prediction and comparison of polymer adhesion whereas equilibrium claiming is not always satisfied when the work of adhesion is calculated using Young-Dupre equation and experimental static contact angles of liquid binders at the solid substrate surfaces;
- taking account of the possible alteration of the polymer adhesive properties caused by solidification of binder;
- existing of possibility of polymer adhesion prediction to polar and non polar model phases both permitting to apply the prediction results for hybrid composite materials.

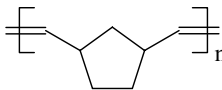
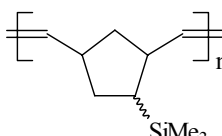
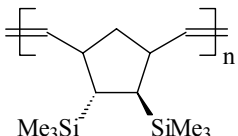
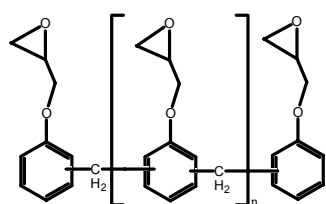
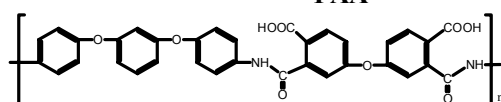
With respect to blood compatibility problem it was exhibited that in system «polymer-water», simulating the «polymer-blood» system, for blood compatible polymer materials must be fulfilled the condition: $\gamma_{S(W)W} \in (1; 3) \text{ mJ}\cdot\text{m}^{-2}$ [10]. If $\gamma_{S(W)W} < 1 \text{ mJ}\cdot\text{m}^{-2}$ the spontaneous dispersing of polymer into water phase occurs, if $\gamma_{S(W)W} > 3 \text{ mJ}\cdot\text{m}^{-2}$ the plasma protein (in particular, fibrinogen) adsorption leads to thrombosis. Two general directions exist to provide the blood compatibility of polymers. There are synthesis of alternating and block copolymers with definite surface morphology due to micro phase separation preventing platelet adhesion and modifying of polymer surface to provide the appropriate value of «polymer-blood plasma» interfacial energy. Three paths exist to realize second direction: the physical adsorption of surfactants or their mixtures, chemisorption of interest compounds

So, the possibilities of contact angle measurement for prediction of possible fields of polymer application and optimization of choice of polymer for the decision of definite practical task mentioned above will be illustrated further on certain examples.

3. EXPERIMENTAL

The films of linear and cross-linked polymers applied onto solid carrier (Alumina plate 10x15x1mm) by glazing from solutions were used (Table 1). Polynorbornenes: non-substituted (PNB), containing one (Me_3Si -PNB) and two ($(\text{Me}_3\text{Si})_2$ -PNB) trimethylsilyl groups in monomer link) were synthesized by ring-opening metathesis polymerization and characterized in A.V.Topchiev Institute of Petrochemical Synthesis, RAS [18].

Table 1. Physical-chemical characteristics of polymers which were objects of investigations.

Structural formula of monomer link	Characteristics of polymers and conditions of films preparation
 PNB	$M_w = 1100000$; $M_w/M_n = 2,2$; cis : trans configuration balance 20 : 80 $T_g = 43^\circ\text{C}$ (Ar) 0,5wt% in toluene; drying in air at 20°C during 2h
 Me_3Si-PNB	$M_w = 500000$; $M_w/M_n = 2,5$; cis : trans configuration balance 30 : 70 $T_g = 102^\circ\text{C}$ (Ar) 0,5wt% in toluene; drying in air at 20°C during 2h
 $(\text{Me}_3\text{Si})_2$-PNB	$M_w = 470000$; $M_w/M_n = 1,9$; cis : trans configuration balance 10 : 90 $T_g = 167^\circ\text{C}$ (Ar) 0,5wt% in toluene; drying in air at 20°C during 2h
ENR 	composition of ENFB in mixture of ethanol : acetone 2:1 and PAA in dimethylformamide; PAA content ω was varied in interval of (0÷10) wt%; subsequent heating at 160°C during 6h of films at Al carrier [19]
PAA 	
Polystyrene PS	$M_w = 43000$; $M_w/M_n = 2,1$; $T_g = 96^\circ\text{C}$ (air) 0,5wt% in toluene

ENFB binder with main ingredient epoxynovolac resin (ENR) was used as received with addition of different amounts of modifying agent of polyamidoacid (PAA) which was a precursor of polyimide [20]. Polystyrene was synthesized by frontal polymerization method and characterized in Institute of Problems of Chemical Physics, RAS [21].

The surfaces of polymer films were standardized using values of water advancing $\theta_a^{(W)}$ and receding $\theta_r^{(W)}$ contact angles. Samples for experiments were chosen so that $\theta_a^{(W)}$ and $\theta_r^{(W)}$ values differs from ones pointed in Table 1 not above ± 1 deg. Contact angles were measured using sessile drop technique at 20°C using horizontal microscope with goniometer at power 20 times with accuracy 1deg.

Two-liquid method (Owens-Wendt-Kaelble)[5] was used to calculate the free surface energy of polymer films γ_{SV} and its dispersive γ_{SV}^d and polar γ_{SV}^p components. The calculations were performed by solving of equation set:

$$\left\{ \begin{array}{l} (1 + \cos \theta_{L1}) \cdot \gamma_{L1} = 2 \left(\sqrt{\gamma_{L1}^d \cdot \gamma_{SV}^d} + \sqrt{\gamma_{L1}^p \cdot \gamma_{SV}^p} \right) \\ (1 + \cos \theta_{L2}) \cdot \gamma_{L2} = 2 \left(\sqrt{\gamma_{L2}^d \cdot \gamma_{SV}^d} + \sqrt{\gamma_{L2}^p \cdot \gamma_{SV}^p} \right) \end{array} \right.$$

where θ_{L1} and θ_{L2} are contact angles of the droplets of test liquids at the polymer surface (Fig.1), γ_{L1}^p , γ_{L2}^p , γ_{L1}^d , γ_{L2}^d – polar and dispersive components of the surface tension of test liquids; $\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p$.

Bidistilled water (W) and ethylene glycol (EG) with purity at least 99.8% with the water content less 0.005% (Sigma Aldrich) were used as test liquids, bidistilled water and octane (O) with purity $\leq 99\%$ (Merck), were used as model liquids [22].

Modified epoxynovolac resin (ER/PAA) was also used as binder for yarn-like micro plastics with inorganic fibers. The micro plastics were prepared using ISO standard [19] (Table 2). Tensile strength of micro plastics was determined also using ISO standard. The tasks of these experiments were to compare the experimentally determined tensile strength with results of prediction of ER/PAA adhesive properties using Wpp and Wdd values and to clarify of the influence of PAA additives on adhesive properties of resin to different fibers. Wpp and Wdd were calculated using Eq.1,2. The Ruckenstein technique was used for $\gamma_{S(W)W}$ and γ_{SO} determination [11,12].

Table 2. Characteristics of micro plastics.

Fiber	Complex filament tensile strength, GPa*	ER/PAA content, wt%	Porosity, %
Basalt	2,30	35 ± 3	$3 \div 5$
Glass	2,45	42 ± 4	$2 \div 5$
UKN	3,20	45 ± 3	$3 \div 6$
Torayca	4,90	33 ± 3	$4 \div 9$

*fabricator's data

To exhibit the possibilities of alteration of $\gamma_{S(W)W}$ using adsorption layers of surfactants¹³ with respect to problem of blood compatibility of polymer materials, the aqueous solutions of following surfactants were used as modifying agents of polystyrene surface: nonionic Pluronic F68 and Tween-80; cationic chlorides of hexadecyltrimethylammonium (CTACl) and hexadecylpyridinium (CPCl); zwitterionic polyelectrolite bovin serum albumin (BSA). It is known that surfactant mixtures can affect with more efficiency in comparison to individual ones [23, 24]. So, the surfactant mixtures were used for modifying of polystyrene surface to provide the desirable $\gamma_{S(W)W}$ value corresponding to Ruckenstein criterion for blood-compatible materials. The surfactant concentrations and compositions of mixtures were chosen on the base of our previous investigations (Table 3) [25, 26].

To control the surfactant adsorption at the polystyrene surface from aqueous solutions Quartz Qrystal Microbalance (QCM) method was applied [26, 27]. To determine the contribution of individual surfactants at summary adsorption on polystyrene from mixed F68/cationic surfactant solutions the original technique was applied [27]. One includes the combination of QCM and radioactive label (RL) methods.

Table 3. Concentrations and compositions of modifying surfactant mixtures.

Mixture	F68/CTACl	F68/CPCl	BSA/Tween-80
Concentration (C) and mole fraction (α) of nonionic surfactant	$C = (10^{-8} \div 5 \cdot 10^{-5})\text{M}$ 0,5	$C = (10^{-8} \div 5 \cdot 10^{-5})\text{M}$ 0,5	$C (\text{Tween-80}) = (4 \cdot 10^{-7} \div 10^{-6})\text{M};$ $C(\text{BSA}) = 10^{-4}\text{M} = \text{const}$

The radioactive tritium label was inserted into CPCl and CTACl molecules by thermal tritium activation method [28]. At first the summary adsorption of F68 and cationic surfactant on polystyrene film was measured by QCM. Then PS film was dissolved in toluene containing scintillator and the quantity of adsorbed labeled cationic surfactant was determined by Liquid Scintillation Counting method.

4. RESULTS AND DISCUSSION

The water wets bad the surfaces of polynorbornenes (Table 4). Wettability is less with content of Me_3Si -substituents in monomer link increase. This result points the hydropobization effect of side Me_3Si -groups in polymer chain caused by screening of π -bonds in polymer chain by substituents. The contact angle hysteresis $\Delta\theta^{(W)}$ value is considerably high; one decreases with increase of Me_3Si -groups. This result is probably connected with more uniform surface package of macromolecules caused by the more uniform isomeric speciation for substituted polynorbornenes. It was shown earlier that PNB is not stable in air atmosphere and one can react with oxygen already at the room temperature [29]. Probably, the highest $\Delta\theta^{(W)}$ value in case of PNB may be conditioned by the minimal stability of this polymer to oxidation during the drying because of relative availability of its π -bonds for oxidation.

¹³ All reagents are from Sigma Aldrich

Table 4. Contact angles of test liquids at the polynorbornenes surfaces.

Polymer	$\theta_a^{(W)}$, deg	$\theta_r^{(W)}$, deg	$\Delta\theta^{(W)}$, deg	$\theta_a^{(EG)}$, deg
PNB	92	77	15	68
Me ₃ Si-PNB	95	83	12	74
(Me ₃ Si) ₂ -PNB	100	93	7	83

The series of polynorbornenes with regular changing structure is very convenient object for interrelation of «structure-surface energetic characteristics- property» of polymer exposure (Table 1). The remarkable tendency of γ_{SV}^d decrease is observed in PNB > Me₃Si-PNB > (Me₃Si)₂-PNB series with polymer density decrease and increase of the coefficients of gas permeability. On the contrary, the γ_{SV}^p keeps a constant value due to tendency of polymer to minimize the specific free surface energy at the interface with non polar air phase. For more hard domain polymers Me₃Si-PNB and (Me₃Si)₂-PNB (Table 1) this effect may be related with screening of π -bonds by Me₃Si-groups. Thus, the results point out the decrease of macromolecules packing density in surface polymer layer and demonstrate the more sensitivity of soft dispersive interactions to its alteration in comparison to inductive and orientation ones.

Table 5. Interrelation between the physical-chemical characteristics and surface energetic characteristics of polynorbornenes.

Polymer	γ_{SV}^d , mJ·m ⁻²	γ_{SV}^p , mJ·m ⁻²	γ_{SV} , mJ·m ⁻²	density ^(a) , g·cm ⁻³	FFV	Gas permeability coefficient, Ba	
						H ₂	O ₂
PNB	20	4	24	0,98	0,16	21 [30]	3 [30]
Me ₃ Si-PNB	15	4	19	0,92	0,20	77 [31]	21 [31]
(Me ₃ Si) ₂ -PNB	12	4	16	0,90	0,22	375 [32]	95 [32]

^(a) hydrostatic weighing method (isopropanol)

The packing density of macromolecules in surface polymer layer may correlate to one inside of polymer phase and other physical-chemical properties related with domain hardness of macromolecule. Really, this interrelation (Table 5) do exists between the polymer density, gas permeability and free volume fraction (FFV). The FFV value was calculated using Bondy's formulae: $FFV = (1 - 1,3 \cdot V_w \cdot d/M)$, where d and M are the density and molar mass of monomer link, V_w is van der Waals volume of monomer link calculated by method of Askadskii [33].

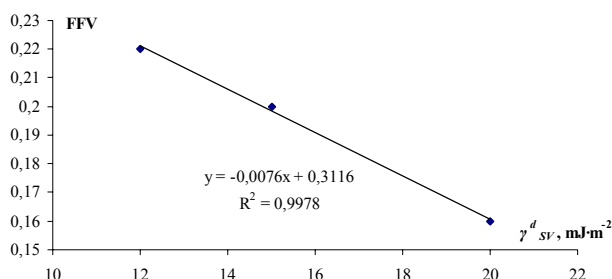


Fig.4. Correlation dependence between FFV and γ_{SV}^d value for polynorbornenes.

Of special note is a good linear dependence between the FFV and γ_{SV}^d values for series of related polymers (polynorbornenes). Concerning such dependence existing for other series of polymers the novel experimental investigations will be done. This result may be in special interest to predict of polymer application for membrane material creation because one exhibits the possibility of express determination of free volume alteration of related polymers with different side groups using contact angle measurements.

The wettability of solidified ENFB/PAA films with water depends on the PAA content (Table 6). The best wettability at $\omega(\text{PAA}) = 3\%$ was observed. With the $\omega(\text{PAA})$ increase in interval $\omega \in (0;10)$ the γ_{SV}^d does not change in its accuracy determination scope (Table 6). At the same time the dependence $\gamma_{SV}^p = f(\omega)$ has maximum at $\omega(\text{PAA}) = 3\%$. Thus, at this composition the ENFB/PAA provide a best adhesion to the test liquids due to the polar interactions.

Table 6. Contact angles of test and model liquids at the ENFB/PAA surfaces at the different PAA content.

$\omega(\text{PAA}), \%$	0	1	2	3	5	7	10
$\theta_a^{(W)}, \text{deg}$	75	71	66	64	68	73	74
$\theta_a^{(EG)}, \text{deg}$	52	48	42	40	45	50	52
θ_V, deg	123	127	135	143	125	124	123
θ_O, deg	103	108	118	127	105	104	103
θ_{WO}, deg	124	126	128	132	128	124	121

The maximums of dependencies of θ_V , θ_O and θ_{WO} from ω at $\omega(\text{PAA}) = 3\%$ also point out the maximal polarity of ENFB/PAA surface at this composition. The $\gamma_{S(W)W}$ minimal value at $\omega(\text{PAA}) = 3\%$ provides the maximal Wpp value due to interaction of ENFB/PAA with model liquid (water) thereby polar interactions. The γ_{SO} does not depend from $\omega(\text{PAA})$. But calculation of Wdd show the maximal adhesion of ENFB/PAA with model liquid (octane) at $\omega(\text{PAA}) = 3\%$ (Table 7).

Table 7. The energetic and adhesion characteristics of ENFB/PAA surfaces at the different PAA content.

$\omega(\text{PAA}), \%$	0	1	2	3	5	7	10
$\gamma_{SV}^d, \text{mJ}\cdot\text{m}^{-2}$	19	18	18	18	18	18	19
$\gamma_{SV}^p, \text{mJ}\cdot\text{m}^{-2}$	13	16	19	21	18	14	13
$\gamma_{SV}, \text{mJ}\cdot\text{m}^{-2}$	32	34	37	39	36	32	32
$\gamma_{S(W)W}, \text{mJ}\cdot\text{m}^{-2}$	8	7	4	2	7	8	8

$\gamma_{so}, \text{mJ}\cdot\text{m}^{-2}$	3	2	2	2	2	3	3
$W_{pp}, \text{mJ}\cdot\text{m}^{-2}$	97	100	106	109	101	97	97
$W_{dd}, \text{mJ}\cdot\text{m}^{-2}$	51	53	57	59	56	51	51

It was founded [20] that such adhesion behavior is provided by the peculiarities of chemical reactions passing during thermo cocuring of ENFB with different PAA content. When $\omega(\text{PAA}) < 5\%$ the cocuring of ENFB and PAA by amide groups of PAA occurs and at $\omega(\text{PAA}) \geq 5\%$, cocuring with the participation of both amide and carboxyl groups of PAA occurs and leads to the formation of a three-dimensional grid of complex structure. Moreover, at $\omega(\text{PAA}) \geq 5\%$ the phase separation in ENFB/PAA during cocuring was observed, perhaps in consequence of polyimide formation at high PAA content [20].

The extremal dependencies of $W_{pp} = f(\omega)$ and $W_{dd} = f(\omega)$ reflect the dependencies of micro plastic tensile strength with ENFB/PAA network from PAA content $P = f(\omega)$ which have maximums at $\omega(\text{PAA}) = 3\%$ independently from fiber type (Fig. 5).

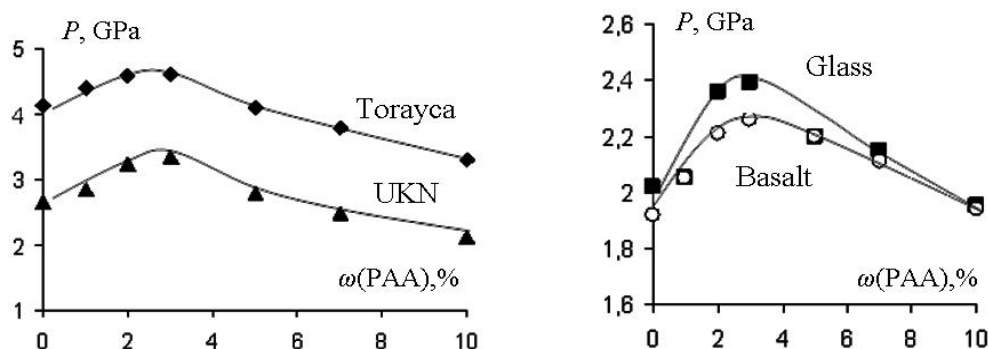


Fig. 5. The dependencies of micro plastics tensile strength P from PAA content in network ω .

Table 8. The influence of adsorption modifying on the interfacial energy of «polystyrene-water» interface.

Conditions	PS	BSA 10^{-4}M	BSA/Tween 80 10^{-4}M	Tween 80 ($4\cdot 10^{-7} \div 10^{-6}$)M	F68/CTACl* 10^{-3}M	F68/CPCl* 10^{-3}M
$\gamma_{S(W)W}, \text{mJ}\cdot\text{m}^{-2}$	19	13	3	1	2	1

* the total surfactant concentration is presented

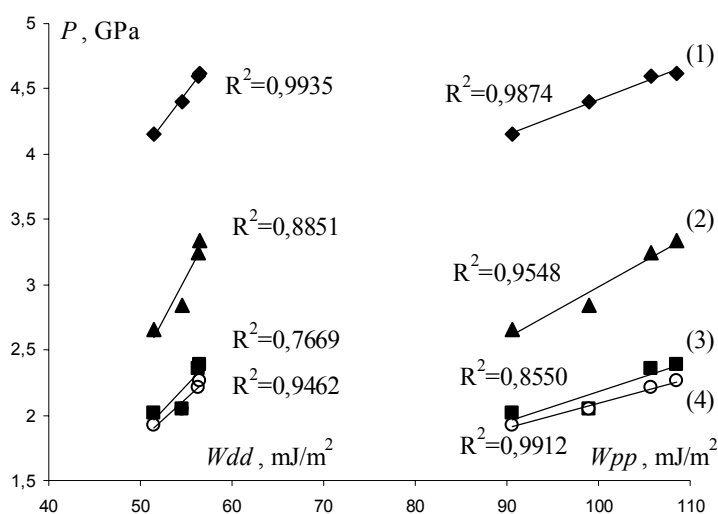


Fig. 6. The correlation dependencies of the work of adhesion of ER/PAA network to model liquids with tensile strength of yarn-like micro plastics with Torayca (1), UKN (2), Glass (3) and Basalt (4) fibers at PAA content $\omega \leq 3\%$.

by polar and non polar intermolecular interactions.

The data of Table 8 demonstrate the possibilities of interfacial energy $\gamma_{S(W)W}$ alteration for blood compatibility providing by means of adsorption modifying of polymer surface using surfactants and their mixtures.

The initial polystyrene surface possesses a bad blood compatibility because of relatively high $\gamma_{S(W)W}$ value. It is known that modifying of surfaces with serum albumin adsorption layers may lead to the blood compatibility if the great conformation changes of adsorbed protein molecules don't occur [25]. But in case of polystyrene the individual adsorption layer of BSA formed from the solution with concentration of BSA $C = 10^{-4}M$ is not able to provide the appropriate $\gamma_{S(W)W}$. Alternately, Tween-80 adsorption layers give too low $\gamma_{S(W)W}$ which induce ones dispergation in the water after the washing of modifying surface with water. This fact was registered using QCM (Fig. 7). The mixed BSA/Tween-80 adsorption layers don't remove from the modified surface after washing while ones provide the $\gamma_{S(W)W}$ value obey to the criterion one for blood compatible materials (Fig.7, Table 8).

It is known that Pluronic adsorption layers may give satisfactory modification effect with respect to for blood compatibility providing of solid surfaces [14]. In order to enough adsorption and strong stability modifying layers at the polymer surface, Pluronics must possess the polyoxypropylene (PPO) chain length containing at least 56 links [14]. In spite of Pluronic F68 has only 30 links in PPO chain, it's significant adsorption can be promoted with cationic surfactants. Presence of CTACl and CPCl in mixtures with F68 also provides stability of mixed adsorption layers during washing by water and satisfactory for blood compatibility $\gamma_{S(W)W}$ value (Table 8).

At the area of homogeneity of ENFB/PAA network a linear correlation between the work of adhesion values and micro plastic tensile strength is observed (Fig. 6). This experimental fact points out on interactions between ENFB/PAA network and inorganic fibers due to polar and dispersion forces both.

So, in case of absence of binder diffusion in fiber the contact angle measurements in a model «polymer-liquid» systems appeared to be able to predict the curing ENFB/PAA composition possessing the maximal adhesive properties realized

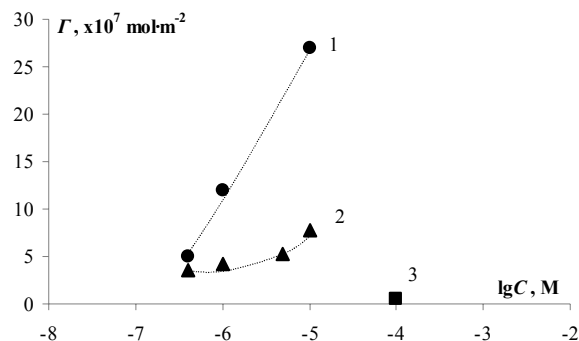


Fig.7. The adsorption (Γ) dependence (QCM) from the Tween-80 concentration (C) for Tween-80 before washing (1), BSA/Tween-80 after washing (2) at $C(\text{BSA}) = \text{const} = 10^{-4}\text{M}$; point (3) corresponds to $\Gamma(\text{BSA})$ at $C(\text{BSA}) = 10^{-4}\text{M}$.

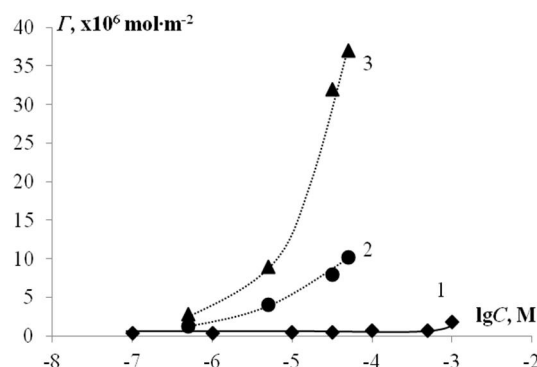


Fig.8. The adsorption (Γ) dependence from the total surfactant concentration (C) for Pluronic F68 (1), F68/CTACl (2) and F68/CPCl (3) mixed solutions ($\alpha = 0,5$): QCM and RL data.

5. CONCLUSIONS

The energetic characteristics of polymer surfaces at the interfaces with air and liquids simulating the polar and non polar media are the convenient parameters which allow predict the possible fields of polymers application for creation of materials. So, for this purpose the contact angle measurements are very informative and relatively express method.

6. ACKNOWLEDGEMENTS

Authors acknowledge the financial support of Russian Foundation for Basic Research (10-03-00222, 11-08-01043). We are grateful to Professor Eugene Shmerovich Finkelshtein and Professor Maria Leonidovna Gringolts for [kindly furnished](#) synthetic polymer samples of metathesis polynorbornenes. We are also grateful to Doctor Ludmila Erikovna Starannikova for the determination of density of polynorbornenes.

7. REFERENCES

1. Adamson A.W. (1976) Physical Chemistry of Surfaces, New York: John Wiley and Sons, 551p.
2. Kloubek J. (1992) Development of methods of surface free energy determination using contact angles of liquids on solids, Adv. in Colloid and Int. Sci., 38, pp. 99-142.
3. De Gen P. G. (1987) Smachivanie: statika i dinamika, 151(4), pp. 619-681, *in russian*.
4. Carre A. (2007) Polar interactions at liquid/polymer interfaces, J. Adhesion Sci. Technol., 21(10), pp. 961-981.
5. Vojtěchovska J. and Kvitek L. (2005) Surface energy – effects of physical and chemical surface properties, Acta Univ. Palacki. Olomuc, Chemica 44, pp. 25-48.

Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 6, Part 2

6. Summ B.D., Gorynov Yu. V. (1986) Fiziko-himicheskie osnovy smachovaniya i rastekaniya, Moskva: Himiya, 232 s., *in russian*.
7. Van Oss C.J., Chaudhury M.K., Good R.G. (1988) Interfacial Lifshits-van der Waals and polar interactions in Macroscopic systems, Chem. Rev., 88, pp. 927-941.
8. Lee L.H. (1996) Correlation between Lewis acid-base surface interaction components and linear solvation energy relationship solvatochromic α and β parameters, Langmuir, 12, pp.1681-1687.
9. Steed J. W., Atwood J. L. (2000) Supramolecular chemistry, John Wiley and Sons, Ltd, pp. 19-34.
10. Ruckenstein E., Gourisankar S.V. (1986) Preparation and characterization of thin film surface coatings for biological environments, Biomaterials, 7, pp. 403-422.
11. Ruckenstein E., Lee S.H. (1987) Estimation of the Equilibrium Surface Free Energy Components of Restructuring Solid Surfaces, J. of Colloid and Interface Sci., 120(1), pp.153-161.
12. Ruckenstein E., Gourisankar S.V. (1985) Environmentally Induced Restructuring of Polymer Surfaces and its influence on their wetting characteristics in an aqueous, J. Colloid Interface Sci., 107(2), pp. 488-502.
13. Bogdanova Yu. G., Dolzhikova V.D. (2009) Fiziko-himicheskie aspekty krovesovmestimosti polimernykh materialov, Sbornik statey XIV vsrossiyskoy konferentsii «Structura I dinamika molekulyarnykh sistem», 3, ss. 4-14, *in russian*.
14. Mansoor A., Kinam P. (1992) Prevention of protein adsorption and platelet adhesion on surfaces by PEO/PPO/PEO triblock copolymers, Biomaterials, 13(10), pp.682-692.
15. Bogdanova Y.G., Dolzhikova V.D., Mazhuga A.G. (2011) Polyolefin ketones adhesive characteristics in model systems polymer-liquid, Polymer Sci., Ser. D, 4(1), pp.8-12.
16. Starostina I.A., Aleeva Y.I., Sechko E.V., Stoyanov O.V. (2009) Encyclopedia of Polymer Composites: Properties, Performance and Applications. New York: Nova Publisers, pp. 681-704.
17. Berger E.J. (1991) Acid-Base Interaction: Relevance to Adhesion Science and Technology / Ed. by K.L. Mittal and H.R. Anderson, Jr. Utrecht: VSP, pp.207-228.
18. Finkelshtein E. Sh. (1995) Metatesisnaya polimerizatsiya nepredel'nykh kremniorganicheskikh, Vysokomol. Soed., 37(4), ss. 718-736.
19. ISO 10618: 2004(E) Carbon fibre – Determination properties of resin-impregnated yarn.
20. Karzov I. M., Alent'ev A. Yu., Bogdanova Yu. G., Kostina Yu. V., Shapagin A. V. (2010) Influence of Energy Characteristics of the Fiber-Binder Interface on Polymer Composite Strength, Moscow University Chemistry Bulletin 65(6), pp. 384-391.
21. Butakov, A. A., Maksimov, E. I. (1973) An experimental study of the heat regimes of tubular reactor, Doklady Akad. Nauk SSSR, 209, pp. 643-646.
22. Bogdanova Yu.G., Dolzhikova V.D., Mazhuga A.G., Shapagin A.V., Chalykh A.E. (2010) Energy characteristics of poly(olefin ketone) surfaces at different interfaces, [Rus. Chem. Bull.](#), 59(7), pp. 1343-1348.
23. Rosen M.J., Gu B. (1987) Synergism in Binary Mixtures of Surfactants, Colloids and Surfaces, 23 (6), pp.119-135.
24. E.D. Goddard (2002) Polymer/Surfactant Interaction: Interfacial Aspects, J. Colloid Interface Sci., 256, pp. 228-235.

Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 6, Part 2

25. Yampol'skaya G.P., Dolzhikova V.D. (2007) Modifikirovanie poverhnosti polistirola kompleksom bychiy syvorotochny albumin-tvin-80 I prognozirovanie biosovmestimosti, Vestn. Mosk. un-ta, Ser. Khim., 48(1), ss. 33-37, *in russian*.
26. Bogdanova Yu.G., Dolzhikova V.D. (2008) Surface and bulk properties of aqueous binary mixed solutions of Pluronic F68 and low-molecular-weight cationic surfactants: 2. Wetting and modifying effects of mixed solutions, 70(2), pp. 144-147.
27. Bogdanova Yu.G., Dolzhikova V.D., Badun G.A., Summ B.D. (2003) Wetting effect of aqueous binary mixed solutions of cationic and nonionic surfactants, [Russ. Chem. Bull.](#), 52(11), pp. C. 2352-2359.
28. Badun G.A., Chernysheva M.G., Tyasto Z.A., Kulikova N.A., Kudryavtsev A.V., Perminova I.V. (2010) A new technique for tritium labeling of humic substances, Radiochimica Acta, 98 (3), pp. 161-166.
29. Finkelshtein E.Sh., Makovetskii K.L., Gringolts M.L., Rogan Yu.V., Golenko T.G., Starannikova L.E., Yampolskii Yu.P., Shantarovich V.P., Suzuki T. (2006) Addition-Type Polynorbornenes with Si(CH₃)₃ Side Groups: Synthesis, Gas Permeability, and Free Volume, Macromolecules, 39(20), pp.7022-7029.
30. Finkelshtein E.Sh., Makovetskii K.L., Yampol'skii Yu.P., Portnykh E B, Ostrovskaya I.Ya., N.E. Kaliuzhnyi, N.A. Pritula, A.I. Golberg, Yatsenko M.S., Plate N.A. (1991) Ring-opening metathesis polymerization of norbornenes. with organosilicon substituents. Gas permeability of polymers obtained, Makromol. Chem., 192 (1), pp.1-9.
31. Finkelshtein E. Sh., Gringolts M.L., Ushakov N.V., Lakhin V.G., Sobolev S.A., Yampol'skii Yu.P. (2003) Synthesis and gas permeation properties of new ROMP polymers from silyl substituted norbornadienes and norbornenes, Polymer, 44, pp. 2843-2851.
32. Yampolskii Yu., Soloviev S.A., Gringolts M.L. (2004) Thermodynamics of sorption in and free volume of poly(5,6-bis(trimethylsilyl)norbornene), Polymer, 45, pp. 6945-6952.
33. Askadskii A.A., Kondraschenko V.I. (1999) Komp'uternoe materialovedenie polimerov. Moskva: Nauchy mir, 544 s., *in russian*.