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Effect of Temperature on Adhesion Work of Model Organic Molecules on Modified Styrene–Divinylbenzene Copolymer Using Inverse Gas Chromatography

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Abstract: In previous studies, a new methodology was developed to determine the free dispersive and polar energies, the surface energies and Lewis acid-base parameters of polystyrene-divinylbenzene (S-DVB) copolymer modified by melamine, 5-Hydroxy-6-methyluracil, and 5-fluouracil. In this paper, we were interested in the determination of the work of adhesion of solvents on the modified copolymer as a function of temperature and for the different modifiers with the help of the inverse gas chromatography at infinite dilution. The variations of the London dispersive and polar surface properties of copolymers against the temperature led to the determination of the different acid-base components of their surface energies. Using Fowkes's equation, van Oss 's relation, and Owens's concept, we obtained the variations of the dispersive and polar works of adhesion of the different solid surfaces as well as the corresponding forces of interaction between the organic solvents and the modified copolymer. It was showed that the work of adhesion is function of two thermodynamic variables: the temperature and the modifier percentage

Keywords: adhesion; adsorption; surfaces and interfaces; Hamieh thermal model; surface enthalpy and entropy of adhesion; Fowkes's equation; van Oss 's method

The study of surface interactions between polymers and solvents is fundamental in many technological and industrial applications such as adsorption, swelling, diffusion, composite fabrication, coatings and adhesives to membrane separations, and adhesion. Polymer surfaces and interfaces play an essential role in many commercial applications of polymers, such as coatings, adhesives, blends, packaging, resists, building, engineering, and biomedical industries. Understanding the interaction processes taking place at interfaces is, therefore, increasingly important for the wide variety of polymer uses. The most important parameter that governs such interfacial interactions is the work of adhesion (W_a), which quantifies the energy required to separate two phases in contact, solid or a liquid solvent, and a solid polymer surface [1,2]. Understanding the thermodynamics and molecular mechanisms that dictate solvent adhesion to polymer or copolymer surfaces is essential for controlling wettability, solvent uptake, film stability, and interfacial compatibility [3,4]. The strength of adhesion to a solid surface can be estimated from a value of the thermodynamic "work of adhesion", W_a, a concept first introduced by Harkins [5] using the various surface tensions intervening when a liquid adheres to a solid.

The adhesion process was described in classical interfacial thermodynamics, using surface tensions and contact angle measurements and utilizing the work of Harkins [5] and the Young-Dupré equation [6,7]. Later, models were proposed by Fowkes [8], Owens-Wendt [9], and van Oss et al.

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[10,11] taking into account intermolecular forces, including dispersive, polar, and acid-base interactions [8–11]. These models provided a more comprehensive understanding of the thermodynamic equilibrium at the solid-liquid interface, especially when dealing with chemically complex or functionalized polymer surfaces.

Polymers and copolymers, such as polystyrene, polymethyl methacrylate (PMMA), and styrene–divinylbenzene (S–DVB) resins, exhibit different chemical functionalities, crosslinking densities, and very interesting morphologies. These properties play a key role in how solvents interact at the surface and in the bulk [12,13]. Moreover, the choice of solvent, characterized by its polarity, hydrogen bonding capacity, and molecular size, directly influences its adsorption behavior and the resulting adhesion energy [13,14]. The synergy between solvent properties and polymer surface energetics thus determines the degree of solvent penetration, polymer swelling, and final desorption dynamics [15].

Despite the crucial role played by adhesion, a rigorous understanding of solvent-polymer adhesion remains elusive due to the complex interplay of a large number of physical, mechanical, thermodynamic, and chemical factors. However, recent advances in experimental techniques, such as contact angle goniometry, isothermal titration calorimetry (ITC), and inverse gas chromatography (IGC), have allowed more precise quantification of adhesion energies and provided a better understanding of solvent-surface interactions at the molecular level [2,12].

In this paper, we aim to provide a new way to determine the work of adhesion of solvents on the surfaces of polymers or copolymers such as polystyrene-divinylbenzene (S-DVB) copolymer modified by several molecules or supramolecules that have had great success in biochemical and pharmaceutical applications. This study is based on the theoretical models that have been validated by experimental results such as the Hamieh thermal model [16–21] and the separation method of the London dispersive and polar free energy of adsorption [22,23] using the well-known inverse gas chromatography (IGC) technique [24–34] at infinite dilution. This research used our new results on the different surface properties of modified copolymers [35–37] to determine the work of adhesion of the various organic model solvents on S-DVB copolymer versus the modifier percentage and the temperature.

2. Materials and Methods

2.1. Materials and Technique

The different organic solvents, modifiers, the S-DVB copolymer, and their origins were described in previous papers [35–37]. The chromatographic measurements of the retention volume of the various organic adsorbed on the modified S-DVB, as well as the IGC technique, and the experimental procedure were the same as those given in previous works [35–37].

2.2. Thermodynamic Methods

2.2.1. Surface Energy Parameters of Modified Copolymers

The application of the Hamieh thermal model allowed obtaining the correct London dispersive surface energy $\gamma_s^d(T)$ of the S-DVB copolymer respectively modified by melamine [35], 5-hydroxy-6-methyluracil [36], and 5-fluouracil [37], for percentages varying from 1% to 10% and the temperature from 443.15 K to 473.15 K. Whereas, the new applied methodology led to the separation between the dispersive free energy $\Delta G_a^0(T)$ and the polar free energy $\Delta G_a^p(T)$ of adsorption of the various organic adsorbed on the modified S-DVB copolymer at different temperatures.

Denoting $\gamma_s^p(T)$ the polar surface energy of the modified copolymer, the total surface energy $\gamma_s(T)$ can be written as follows:

$$\gamma_s(T) = \gamma_s^d(T) + \gamma_s^p(T) \tag{1}$$

Applying the Van Oss et al.'s method [11] to the modified copolymers, it was possible to obtain the different values of the Lewis acid γ_s^+, and base γ_s^- surface energies using the following expression of $\Delta G_a^p(T)$ and the well-known surface parameters of two polar solvents such as ethyl acetate and dichloromethane:

$$-\Delta G_a^p(T) = 2\mathcal{N}a(T)\left(\sqrt{\gamma_l^-\gamma_s^+} + \sqrt{\gamma_l^+\gamma_s^-}\right) \qquad (2)$$

Equation (2) led to the values of the acid-base surface energy γ_s^{AB} or γ_s^p of the solid surfaces with the help of Relation (3):

$$\gamma_s^{AB} = \gamma_s^p = 2\sqrt{\gamma_s^+\gamma_s^-} \qquad (3)$$

2.2.2. Surface Energy and Work of Adhesion

Considering a liquid of known surface tension $\boldsymbol{\gamma_l}$ in contact with a simple solid, smooth, homogeneous, non-deformable and isotropic surface, the corresponding work of adhesion $\boldsymbol{W_a}$ can be then written as:

$$\boldsymbol{W_a = \gamma_s + \gamma_l - \gamma_{sl}} \qquad (4)$$

Where $\boldsymbol{\gamma_{sl}}$ is the solid/liquid interface tension.

Young [38] proposed the following equation:

$$\boldsymbol{\gamma_l \, cos\theta = \gamma_s - \gamma_{sl}} \qquad (5)$$

by defining the concept of the contact angle $\boldsymbol{\theta}$ formed between the liquid drop and the plan solid surface.

Whereas, Dupré [7] used the Young's equation and expressed the work of adhesion by Equation (6):

$$\boldsymbol{W_a = \gamma_l \,(1 + cos\theta)} \qquad (6)$$

Fowkes [8] applied the geometric mean of the dispersive components of the solid and liquid and proposed a new expression of the work of adhesion:

$$\boldsymbol{W_a = \gamma_l \,(1 + cos\theta) = 2\sqrt{\gamma_s^{\mathrm{d}}\gamma_l^{\mathrm{d}}}} \qquad (7)$$

where Equation (7) is only valid for dispersive interactions.

Later, the Fowkes's equation [8] was extended to an approach taking into account the polar contribution (hydrogen bonding) [9] in the expression of the work adhesion:

$$\boldsymbol{W_a = 2\sqrt{\gamma_s^{\mathrm{d}}\gamma_l^{\mathrm{d}}} + 2\sqrt{\gamma_s^{\mathrm{p}}\gamma_l^{\mathrm{p}}}} \qquad (8)$$

The values of γ_s^p and the Lewis acid γ_s^+, and base γ_s^- surface energies of solid copolymers were obtained using Van Oss et al.'s method [10] and applying Equation (9):

$$-\Delta G_a^p(T) = 2\mathcal{N}a(T)\left(\sqrt{\gamma_l^-\gamma_s^+} + \sqrt{\gamma_l^+\gamma_s^-}\right) \qquad (9)$$

This allowed obtaining the polar (or acid–base) surface energy γ_s^{AB} of the modified copolymers using Equation (10):

$$\gamma_s^{AB} = \gamma_s^p = 2\sqrt{\gamma_s^+\gamma_s^-} \qquad (10)$$

Therefore, the work of adhesion can be expressed as follows:

$$W_a = 2\left[\sqrt{\gamma_s^{\mathrm{d}}\gamma_l^{\mathrm{d}}} + \sqrt{\gamma_l^-\gamma_s^+} + \sqrt{\gamma_l^+\gamma_s^-}\right] \qquad (11)$$

The different surface energy components of the modified copolymers were previously determined, it was then possible to calculate the work of adhesion with the help of Equations (11).

Furthermore, the dispersive $W_a^{\mathrm{d}}(T)$ and polar $W_a^{\mathrm{p}}(T)$ contributions of the work of adhesion can be written as follows:

$$\begin{cases} W_a(T) = W_a^{\mathrm{d}}(T) + W_a^{\mathrm{p}}(T) \\ W_a^{\mathrm{d}}(T) = 2\sqrt{\gamma_s^{\mathrm{d}}(T)\gamma_l^{\mathrm{d}}(T)} \\ W_a^{\mathrm{p}}(T) = 2\left[\sqrt{\gamma_l^- \gamma_s^+} + \sqrt{\gamma_l^+ \gamma_s^-}\right] = 2\sqrt{\gamma_l^{\mathrm{p}}(T)\gamma_s^{\mathrm{p}}(T)} \end{cases} \tag{12}$$

3. Results

3.1. London Dispersive Surface Energy of Modified Copolymers

Based on the Hamieh thermal model [22,24] and the Fowkes's equation [8], the representation of the variations of $RTlnV_n(T)$ of n-alkanes adsorbed on the modified copolymers as a function of $2\mathcal{N}a(T)\left(\gamma_l^d(T)\right)^{1/2}$ led to $\gamma_s^d(T)$ of the various copolymers against the temperatures [H1-H3]. The results were plotted in Figure 1 where a decrease of $\gamma_s^d(T)$ was observed as the temperature increased. The highest London dispersive surface energy was obtained with 1% melamine / S-DVB closest to $\gamma_s^d(T)$ of the copolymer alone, while the lowest values were shown with 10% 5-HMU / S-DVB. An important difference in $\gamma_s^d(T)$ of the copolymer behavior was found affected both by the modifier and its percentage. Figure 1 clearly showed a decrease in the values of $\gamma_s^d(T)$ of S-DVB when it was modified by 5-HMU or 5-FU certainly due to the morphology change in the copolymer structure.

The different linear equations of $\gamma_s^d(T)$ function of the temperature, were given in Table 1 with the values of the surface entropy and the maximum temperature of the various modified copolymers. The results in Table 1 proved a difference in the various surface thermodynamic variables of the modified copolymers. Furthermore, the abnormally high values of the London dispersive surface extrapolated at 298.15K observed in Table 1 are mainly due to the nonlinear variations of $\gamma_s^d(T)$ of the solid surfaces for lower temperatures resulted in the important change in the surface groups of the copolymers when the temperature undergoes severe variations from 475.15K to 298.15K.

Table 1. Equations of $\gamma_s^d(T)$ of S-DVB-L-285 varying the percentage of 5-hydroxy-6-methyluracil, the linear regression coefficients R^2, the London dispersive surface entropy ε_s^d, the values of London dispersive surface energy extrapolated at 0 K and 298.15 K, and the temperature maximum T_{Max}, using the Hamieh thermal model.

Copolymer	Equation of $\gamma_s^d(T)$ (mJ/m^2)	R^2	$-\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m^{-2} K^{-1})	$\gamma_s^d(T = 0K)$ (mJ/m^2)	$\gamma_s^d(T = 298.15K)$ (mJ/m^2)	T_{Max} (K)
S+DVB	$\gamma_s^d(T)= -1.105\ T + 587.13$	0.9980	0.835	587.13	257.7	531.4
1% Melamine/ S-DVB	$\gamma_s^d(T)= -0.907\ T + 496.21$	0.9972	0.907	496.21	225.79	547.1
2% Melamine/ S-DVB	$\gamma_s^d(T)= -0.656\ T + 341.59$	0.9590	0.656	341.59	146.12	521.0
3% Melamine/ S-DVB	$\gamma_s^d(T)= -0.827\ T + 439.96$	0.9608	0.827	439.96	193.51	532.3
4% Melamine/ S-DVB	$\gamma_s^d(T)= -0.876\ T + 473.64$	0.975	0.876	473.64	212.40	540.6
5% Melamine/ S-DVB	$\gamma_s^d(T)= -0.935\ T + 501.23$	0.9825	0.935	501.23	222.46	536.07
10% Melamine/ S-DVB	$\gamma_s^d(T)= -1.220\ T + 584.42$	0.9915	1.220	584.42	220.68	479.03
Copolymer	Equation of $\gamma_s^d(T)$ (mJ/m^2)	R^2	$-\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m^{-2} K^{-1})	$\gamma_s^d(T = 0K)$ (mJ/m^2)	$\gamma_s^d(T = 298.15K)$ (mJ/m^2)	T_{Max} (K)
1% HMU/ S-DVB	$\gamma_s^d(T) = -0.874\ \mathrm{T} + 444.68$	0.9837	0.874	444.68	184.16	508.9
3.5% HMU/ S-DVB	$\gamma_s^d(T) = -1.096\ \mathrm{T} + 544.23$	0.9886	1.096	544.23	217.52	496.7
5% HMU/ S-DVB	$\gamma_s^d(T) = -1.120\ \mathrm{T} + 552.77$	0.9973	1.198	552.77	218.84	493.6
10% HMU/ S-DVB	$\gamma_s^d(T) = -1.198\ \mathrm{T} + 582.13$	0.9973	1.198	582.13	224.95	485.9
Copolymer	Equation of $\gamma_s^d(T)$ (mJ/m^2)	R^2	$-\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m^{-2} K^{-1})	$\gamma_s^d(T = 0K)$ (mJ/m^2)	$\gamma_s^d(T = 298.15K)$ (mJ/m^2)	T_{Max} (K)
1% 5-FU / S-DVB	$\gamma_s^d(T) = -0.497\ \mathrm{T} + 290.95$	0.8900	0.497	290.95	142.77	585.4
5% 5-FU / S-DVB	$\gamma_s^d(T) = -0.780\ \mathrm{T} + 424.67$	0.9800	0.780	424.67	192.11	544.4
10% 5-FU / S-DVB	$\gamma_s^d(T) = -0.913\ \mathrm{T} + 490.08$	0.9900	0.913	490.08	217.87	536.8

Table 1 showed that the different values of -ε_s^d, $\gamma_s^d(T = 0\ \mathrm{K})$, and $\gamma_s^d(T = 298.15\ \mathrm{K})$, increased when the percentage of 5-hydroxy-6-methyluracil increased. This also showed an important effect of the surface groups of the copolymer on the London dispersive surface parameters. However, a decrease was observed in the values of T_{Max} when the modifier percentage increased certainly due to the decrease of $\gamma_s^d(T)$ for higher temperatures.

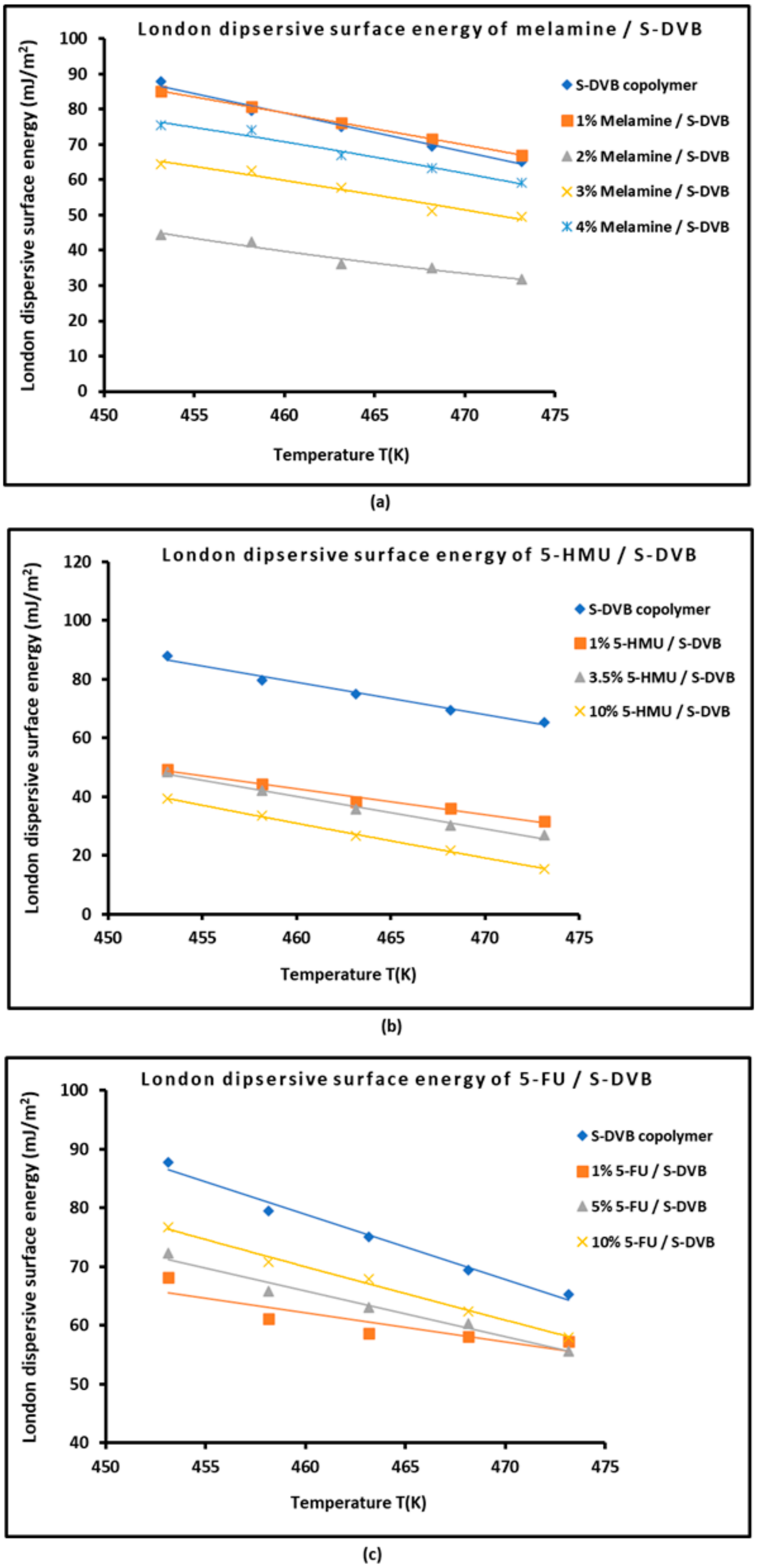


Figure 1. Variations in the London dispersive surface energy of copolymers modified by different molecules versus the temperature. Melamine / S-DVB (a), 5-HMU / S-DVB, and 5-FU / S-DVB for different percentages of modifier.

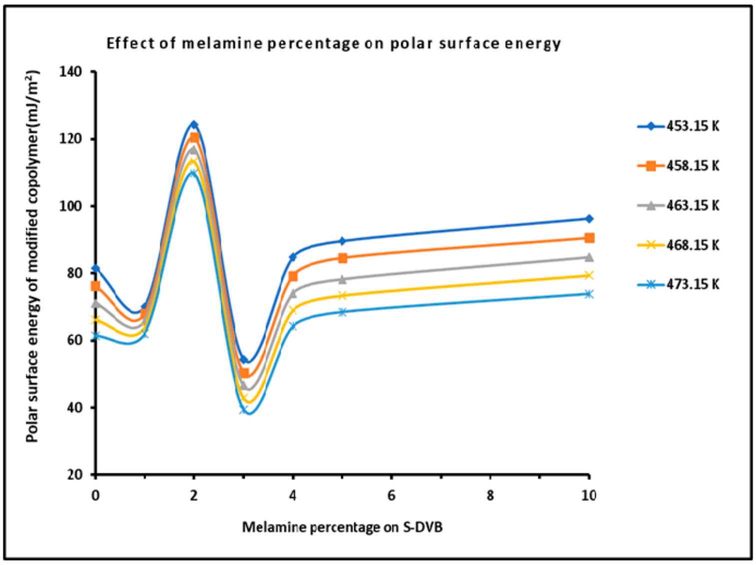
3.2. Polar (Lewis Acid–Base) Surface Energy of Modified Copolymers

First, the polar acid γ_s^+ and base γ_s^- surface energies of modified copolymers were obtained using the method of van Oss et al. [10]. This led to the values of the polar surface energy γ_s^p and consequently to those of the total surface energy $\gamma_s^{tot.}$ obtained as a function of temperature using the previous equations and the results of $\gamma_s^d(T)$. The values of $\gamma_s^p(T)$ of the copolymers were given in Table 2. They showed that the modifier 2% melamine on S-DVB copolymer exhibited the highest polar surface energy followed by 5% 5-Fu / S-DVB. Whereas the lowest $\gamma_s^p(T)$ was observed with 1% 5-Fu / S-DVB. The results in Table 2 clearly showed the large effect of the temperature and the modifier on the polar surface energy.

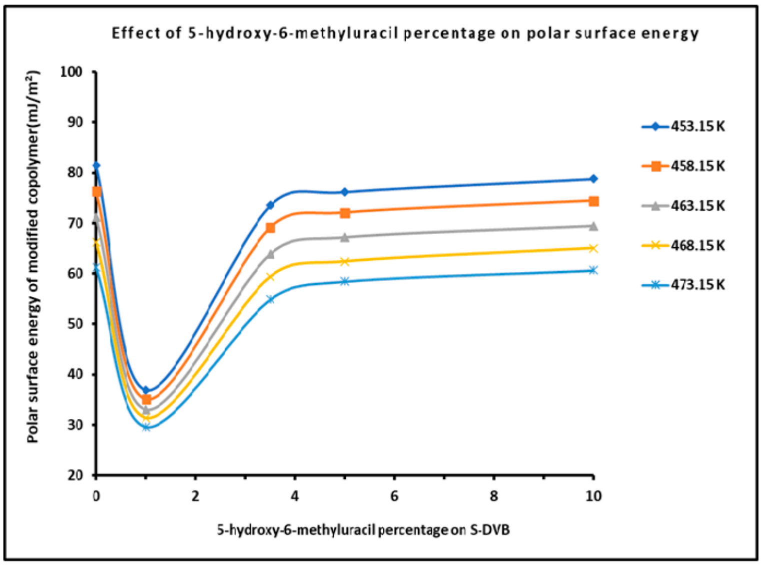
Table 2. Variations of polar surface energy $\gamma_s^p(T)$ (in mJ/m²) of modified copolymers avec the corresponding linear equations.

Temperature T(K)	**453.15**	**458.15**	**463.15**	**468.15**	**473.15**	**Equation $\gamma_s^p(T)$**	**R²**
S-DVB copolymer	81.54	76.29	71.17	66.19	61.33	$\gamma_s^p(T)$= -1.0104 T + 539.27	0.9998
1% Melamine / S-DVB	70.11	68.03	65.99	64	62.07	$\gamma_s^p(T)$= -0.4022 T + 252.32	0.9998
2% Melamine / S-DVB	124.35	120.53	116.81	113.18	109.63	$\gamma_s^p(T)$= -0.7358 T + 457.69	0.9998
3% Melamine / S-DVB	54.36	50.34	46.51	42.87	39.41	$\gamma_s^p(T)$= -0.7474 T + 392.86	0.9991
4% Melamine / S-DVB	84.71	79.24	73.99	68.97	64.16	$\gamma_s^p(T)$= -1.0274 T + 550.05	0.9994
Temperature T(K)	**453.15**	**458.15**	**463.15**	**468.15**	**473.15**	**Equation $\gamma_s^p(T)$**	**R²**
1% 5-HMU / S-DVB	36.89	35.08	33.04	31.34	29.61	$\gamma_s^p(T)$= -0.366 T + 202.7	0.9990
3.5% 5-HMU / S-DVB	73.56	69.12	63.85	59.40	54.90	$\gamma_s^p(T)$= -0.9408 T + 499.9	0.9992
10% 5-HMU / S-DVB	78.82	74.47	69.42	65.06	60.66	$\gamma_s^p(T)$= -0.9146 T + 493.28	0.9994
Temperature T(K)	**453.15**	**458.15**	**463.15**	**468.15**	**473.15**	**Equation $\gamma_s^p(T)$**	**R²**
1% 5-FU / S-DVB	23.61	21.01	18.60	16.35	14.28	$\gamma_s^p(T)$= -0.4664 T + 234.78	0.9980
5% 5-FU / S-DVB	105.08	96.96	89.26	81.96	75.06	$\gamma_s^p(T)$= -1.5008 T + 784.76	0.9990
10% 5-FU / S-DVB	98.84	93.37	88.12	83.08	78.23	$\gamma_s^p(T)$= -1.0302 T + 565.47	0.9994

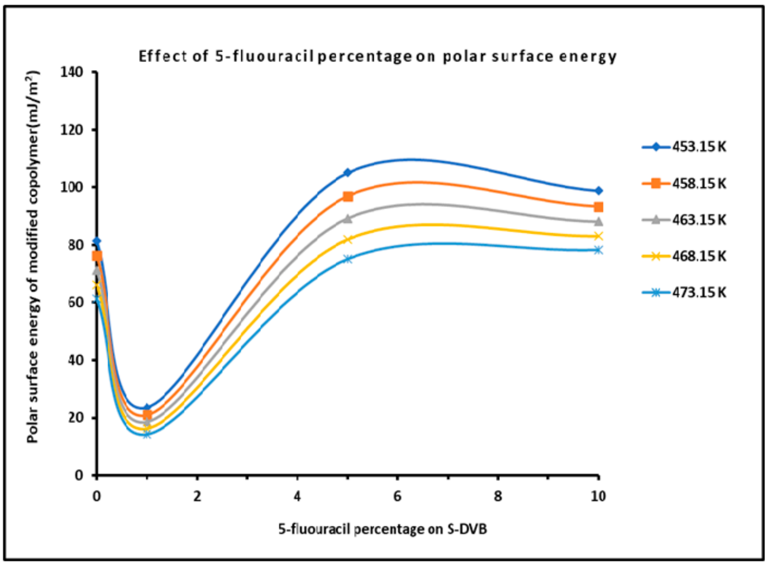
To highlight the effect of the modifier percentage on γ_s^p of the different modified copolymers, the curves of γ_s^p of solid surfaces were drawn in Figure 2 as a function of the modifier percentage. The variations of γ_s^p for all used modifiers are not linear when the modifier percentage varies. A maximum of γ_s^p was observed at 2% melamine / S-DVB and a minimum at 3% of melamine for all temperatures with a pallier after 4% melamine (Figure 2a). However, a minimum of γ_s^p was observed at 1% of 5-HMU (Figure 2b.) and 5-FU (Figure 2c.) for the different temperatures and a pallier shown in Figure 2 after 4% of modifier on S-DVB copolymer. The results thus proved that the polar surface energy is strongly affected not only by the temperature but also by both the nature and the percentage of the modifier as it was shown in Figure 3. It seems that the S-DVB copolymer modified by melamine gives the highest γ_s^p at 2% melamine, while the 5-Fu on S-DVB exhibits the highest γ_s^p after 4% 5-Fu.



(a)



(b)



(c)

Figure 2. Variations of the polar surface energy γ_s^p of the different modified copolymers as a function of modifier percentage at various temperatures. Melamine / S-DVB (a), 5-HMU /S-DVB (b), and 5-FU / S-DVB.

3.3. Polar Surface Energy of Organic Solvents

The polar free energy $-\Delta G_a^p(T)$ of adsorption of solvents on the various copolymers can be also written as:

$$-\Delta G_a^p(T) \;=\; 2\mathcal{N}a(T)\sqrt{\gamma_l^{\mathrm{p}}(T)\gamma_s^{\mathrm{p}}(T)} \qquad (13)$$

Where $\gamma_l^{\mathrm{p}}(T)$ is the polar surface energy of the solvents depending on temperature.

The variations of $-\Delta G_a^p(T)$ of the various polar solvents versus the temperature were previously determined [35–37]. Knowing the values of $\gamma_s^{\mathrm{p}}(T)$ of the various copolymers and those of the surface area of the different organic molecules [16–23], the variations of $\gamma_l^{\mathrm{p}}(T)$ were directly obtained using Equation (13). The results were plotted in Figure S1. The curves in Figure S1 showed linear variations of $\gamma_l^{\mathrm{p}}(T)$ of the different polar solvents versus the temperature. The different equations of $\gamma_l^{\mathrm{p}}(T)$ were given in Table 3.

Results in Figure S1 and Table 3 highlighted the important dependence of $\gamma_l^{\mathrm{p}}(T)$ both on the temperature and the modifier percentage. It was shown that the polar surface energy of ethanol, propanol, i-propanol, and n-butanol, i-butanol and n-pentanol gave the highest values whereas cyclohexane, benzene, and toluene exhibited the lowest $\gamma_l^{\mathrm{p}}(T)$. Of course, the presence of hydroxyl group in these solvents strengthens their polarity relative to other polar molecules.

Table 3. Equations of $\gamma_l^{\mathrm{p}}(T)$ (in mJ/m^2) of the various polar solvents adsorbed on the modified copolymers with the linear regression coefficients.

S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{p}}(T)$**	**R²**
cyclohexane	$\gamma_l^{\mathrm{p}}(T) = 4\times10^{-4}\,T - 0.116$	0.9909
benzene	$\gamma_l^{\mathrm{p}}(T) = 3\times10^{-5}\,T - 0.010$	0.9911
toluene	$\gamma_l^{\mathrm{p}}(T) = -0.0022\,T + 1.048$	0.9984
ethyl acetate	$\gamma_l^{\mathrm{p}}(T) = -0.0251\,T + 14.11$	0.9999
ethanol	$\gamma_l^{\mathrm{p}}(T) = -0.180\,T + 90.12$	0.9999
n-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.063\,T + 30.01$	0.9905
i-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.111\,T + 55.49$	0.9999
n-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.019\,T + 9.124$	0.9958
i-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.054\,T + 28.21$	0.9999
n-pentanol	$\gamma_l^{\mathrm{p}}(T) = -0.0032\,T + 1.766$	0.9995
i-pentanol	$\gamma_l^{\mathrm{p}}(T) = -0.020\,T + 11.360$	0.9994
Pyridine	$\gamma_l^{\mathrm{p}}(T) = -0.065\,T + 33.38$	1
Dichloromethane	$\gamma_l^{\mathrm{p}}(T) = 0.094\,T - 33.51$	0.9906
1% melamine/S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{p}}(T)$**	**R²**
cyclohexane	$\gamma_l^{\mathrm{p}}(T) = 6\times10^{-5}\,T - 0.003$	0.9999
benzene	$\gamma_l^{\mathrm{p}}(T) = -6\times10^{-5}\,T + 0.035$	1
toluene	$\gamma_l^{\mathrm{p}}(T) = -8\times10^{-4}\,T + 0.437$	0.9999
ethyl acetate	$\gamma_l^{\mathrm{p}}(T) = -0.004\,T + 4.024$	0.9999
ethanol	$\gamma_l^{\mathrm{p}}(T) = -0.205\,T + 105.85$	0.9998
n-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.122\,T + 60.84$	0.9992
i-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.076\,T + 36.61$	0.9966
n-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.059\,T + 29.78$	0.9997
i-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.030\,T + 14.080$	0.9846

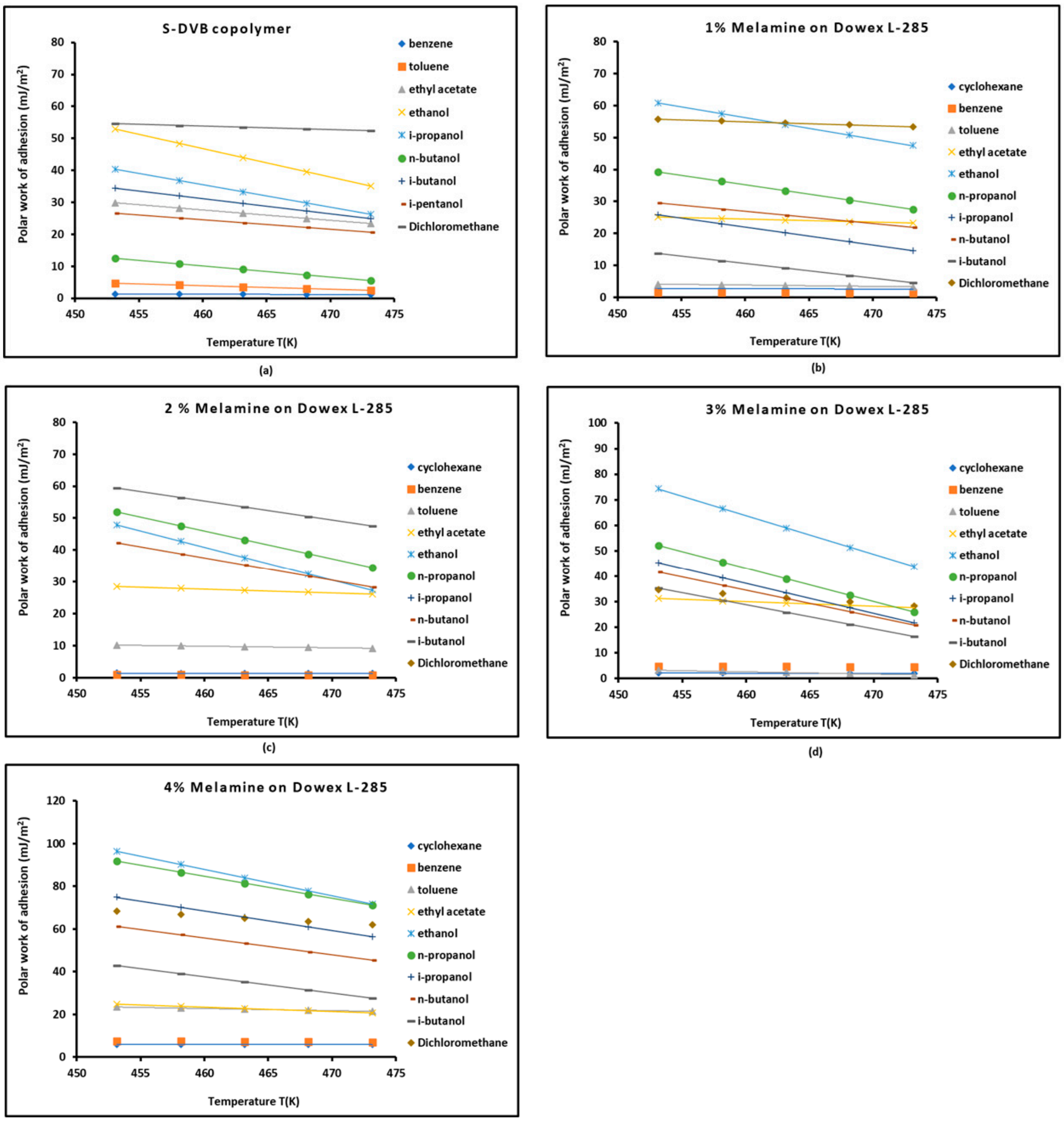
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = 0.020\,T + 2.037$	0.9995
2% melamine/S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{P}}(T)$**	**R²**
cyclohexane	$\gamma_l^{\mathrm{P}}(T) = -2\times10^{-5}\,T + 0.013$	0.9999
benzene	$\gamma_l^{\mathrm{P}}(T) = -3\times10^{-5}\,T + 0.016$	0.9999
toluene	$\gamma_l^{\mathrm{P}}(T) = -8\times10^{-4}\,T + 0.561$	0.9999
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = -0.004\,T + 3.351$	0.9999
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.145\,T + 70.16$	0.9966
n-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.136\,T + 66.86$	0.9987
i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.147\,T + 99.70$	0.9999
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.088\,T + 43.58$	0.9989
i-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.097\,T + 50.92$	1
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = 0.037\,T - 1.415$	0.9995
3% melamine/S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{P}}(T)$**	**R²**
cyclohexane	$\gamma_l^{\mathrm{P}}(T) = 2\times10^{-4}\,T - 0.050$	0.9977
benzene	$\gamma_l^{\mathrm{P}}(T) = 0.0012\,T - 0.452$	0.9969
toluene	$\gamma_l^{\mathrm{P}}(T) = -0.0017\,T + 0.825$	0.9978
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = 0.020\,T - 4.373$	0.9979
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.662\,T + 325.2$	0.9999
n-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.409\,T + 197.56$	0.999
i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.325\,T + 156.67$	0.9985
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.263\,T + 126.86$	0.9991
i-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.201\,T + 96.57$	0.9984
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = -0.022\,T + 15.682$	0.9996
4% melamine/S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{P}}(T)$**	**R²**
cyclohexane	$\gamma_l^{\mathrm{P}}(T) = 0.002\,T - 0.587$	0.9971
benzene	$\gamma_l^{\mathrm{P}}(T) = 0.002\,T - 0.497$	0.9978
toluene	$\gamma_l^{\mathrm{P}}(T) = 0.008\,T - 2.192$	0.9983
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = -0.007\,T + 4.91$	0.9992
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.371\,T + 195.72$	0.9998
n-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.253\,T + 139.54$	0.9995
i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.210\,T + 111.55$	0.9997
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.154\,T + 80.89$	0.9997
i-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.124\,T + 61.62$	1
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = 0.057\,T - 11.874$	0.9973
1% 5-HMU/S-DVB		
Solvents	**Equation $\gamma_l^{\mathrm{P}}(T)$**	**R²**
benzene	$\gamma_l^{\mathrm{P}}(T) = 3\times10^{-5}\,T + 0.008$	0.9914
toluene	$\gamma_l^{\mathrm{P}}(T) = -0.043\,T + 24.09$	0.9891
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = 0.036\,T - 3.586$	0.9981
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.292\,T + 140.76$	0.9961

i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.090\,T + 42.2$	0.9287
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.210\,T + 103.05$	0.9992
i-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.124\,T + 60.03$	0.9973
i-pentanol	$\gamma_l^{\mathrm{P}}(T) = -0.121\,T + 60.29$	0.9998
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = -0.005\,T + 4.348$	0.9983
	3.5% 5-HMU/S-DVB	
Solvents	**Equation** $\boldsymbol{\gamma_l^{\mathrm{P}}(T)}$	**R²**
benzene	$\gamma_l^{\mathrm{P}}(T) = 4\times10^{-4}\,T - 0.156$	0.9935
toluene	$\gamma_l^{\mathrm{P}}(T) = -4\times10^{-4}\,T + 0.542$	0.9988
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = 0.183\,T - 58.14$	0.9938
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.248\,T + 130.23$	0.9997
i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.139\,T + 82.08$	0.9985
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.1274\,T + 72.60$	0.9983
i-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.105\,T + 62.56$	0.998
i-pentanol	$\gamma_l^{\mathrm{P}}(T) = 0.047\,T + 14.09$	0.9983
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = -0.0070\,T + 4.119$	0.9998
	10% 5-HMU/S-DVB	
Solvents	**Equation** $\boldsymbol{\gamma_l^{\mathrm{P}}(T)}$	**R²**
benzene	$\gamma_l^{\mathrm{P}}(T) = 0.0017\,T - 0.588$	0.9942
toluene	$\gamma_l^{\mathrm{P}}(T) = 0.013\,T - 3.856$	0.9949
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = 0.183\,T - 59.09$	0.9945
ethanol	$\gamma_l^{\mathrm{P}}(T) = -0.150\,T + 113.86$	0.9995
i-propanol	$\gamma_l^{\mathrm{P}}(T) = 0.154\,T - 9.398$	0.995
n-butanol	$\gamma_l^{\mathrm{P}}(T) = -0.097\,T + 52.92$	0.9993
i-butanol	$\gamma_l^{\mathrm{P}}(T) = 0.162\,T - 21.42$	0.996
i-pentanol	$\gamma_l^{\mathrm{P}}(T) = -0.074\,\mathrm{T} + 37.042$	1
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = -0.008\,T + 4.491$	0.9999
	1% 5-FU/S-DVB	
Solvents	**Equation** $\boldsymbol{\gamma_l^{\mathrm{P}}(T)}$	**R²**
benzene	$\gamma_l^{\mathrm{P}}(T) = 0.0016\,T - 0.668$	0.9905
toluene	$\gamma_l^{\mathrm{P}}(T) = 0.015\,T - 5.243$	0.9945
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = -0.020\,T + 30.52$	0.987
ethanol	$\gamma_l^{\mathrm{P}}(T) = 0.882\,T - 276.34$	0.9948
i-propanol	$\gamma_l^{\mathrm{P}}(T) = -0.021\,T + 76.68$	0.8954
n-butanol	$\gamma_l^{\mathrm{P}}(T) = 0.862\,\mathrm{T} - 304.64$	0.9947
i-butanol	$\gamma_l^{\mathrm{P}}(T) = 0.965\,\mathrm{T} - 334.37$	0.995
i-pentanol	$\gamma_l^{\mathrm{P}}(T) = -0.520\,T + 259.83$	0.9995
Dichloromethane	$\gamma_l^{\mathrm{P}}(T) = 0.001\,T + 0.671$	0.9858
	5% 5-FU/S-DVB	
Solvents	**Equation** $\boldsymbol{\gamma_l^{\mathrm{P}}(T)}$	**R²**
benzene	$\gamma_l^{\mathrm{P}}(T) = 2\times10^{-4}\,T - 0.074$	0.9967
toluene	$\gamma_l^{\mathrm{P}}(T) = 0.016\,T - 4.833$	0.9979
ethyl acetate	$\gamma_l^{\mathrm{P}}(T) = 0.003\,T + 19.418$	0.9717

ethanol	$\gamma_l^{\mathrm{p}}(T) = -0.175\,T + 84.021$	0.9983
i-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.175\,T + 116.52$	0.9974
n-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.219\,\mathrm{T} + 121.67$	0.9985
i-butanol	$\gamma_l^{\mathrm{p}}(T) = 0.160\,T - 9.321$	0.9997
i-pentanol	$\gamma_l^{\mathrm{p}}(T) = -0.003\,T + 31.15$	0.9386
Dichloromethane	$\gamma_l^{\mathrm{p}}(T) = -0.0002\,\mathrm{T} + 1.280$	0.9714
	10% 5-FU/S-DVB	
Solvents	**Equation $\gamma_l^{\mathrm{p}}(T)$**	**R²**
benzene	$\gamma_l^{\mathrm{p}}(T) = 1\times10^{-4}\,T - 0.036$	0.9986
toluene	$\gamma_l^{\mathrm{p}}(T) = 0.063\,T - 17.82$	0.9988
ethyl acetate	$\gamma_l^{\mathrm{p}}(T) = -0.073\,T + 65.639$	0.9991
ethanol	$\gamma_l^{\mathrm{p}}(T) = -0.2547\,T + 124.57$	0.9992
i-propanol	$\gamma_l^{\mathrm{p}}(T) = -0.326\,T + 211.43$	0.9992
n-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.318\,\mathrm{T} + 176.42$	0.9996
i-butanol	$\gamma_l^{\mathrm{p}}(T) = -0.192\,\mathrm{T} + 93.24$	0.9989
i-pentanol	$\gamma_l^{\mathrm{p}}(T) = -0.347\,T + 213.6$	0.9999
Dichloromethane	$\gamma_l^{\mathrm{p}}(T) = 0.002\,T - 0.057$	0.9981

3.4. Work of Adhesion of Organic Solvents on Modified Copolymer

The determination of the London dispersive and polar surface energies of the various modified copolymers as well as the values of polar surface energy of adsorbed solvents led using the Equations (12) to the values of dispersive $W_a^{\mathrm{d}}(T)$, polar $W_a^{\mathrm{p}}(T)$, and total work $W_a(T)$ of adhesion between solvents and the various solid surfaces by varying the temperature, the modifier, and its percentage. The variations of $W_a^{\mathrm{d}}(T)$ were plotted in Figures S2 as a function of temperature for all copolymers and modifiers at different percentages. Whereas the evolution of $W_a^{\mathrm{p}}(T)$ versus the temperature was drawn in Figures 3. An excellent linearity of the curves $W_a^{\mathrm{d}}(T)$ and $W_a^{\mathrm{p}}(T)$ was observed in Figures S2 and Figures 2 for all solvents and solid materials. A general decrease was noticed against the temperature for the two dispersive and polar works of adhesion with different behaviors depending on the modifier nature and its percentage. It was shown in Figure 3 that the polar adhesion work of ethanol on S-DVB modified by melamine was the highest while that of benzene and toluene was the lowest where a minimum of polar adhesion has been noticed confirming the lowest values obtained in adsorption of these solvents on the modified copolymer. However, in the case of the modification of S-DVB by 5-HMU, the polar work of adhesion $W_a^{\mathrm{p}}(T)$ of ethyl acetate was the highest for 1% and 3.5% of 5-HMU, while that of i-propanol gave the highest $W_a^{\mathrm{p}}(T)$ for 10% 5-HMU, 1% 5-FU and 5% 5-FU. Furthermore, the comparison between the various modifiers led to conclude using Figure S3 that the maximum of adhesion work was obtained with 5-FU.


S-DVB copolymer
Polar work of adhesion (mJ/m²)
Temperature T(K)
benzene
toluene
ethyl acetate
ethanol
i-propanol
n-butanol
i-butanol
i-pentanol
Dichloromethane
1% Melamine on Dowex L-285
cyclohexane
benzene
toluene
ethyl acetate
ethanol
n-propanol
i-propanol
n-butanol
i-butanol
Dichloromethane
2 % Melamine on Dowex L-285
3% Melamine on Dowex L-285
4% Melamine on Dowex L-285
0
10
20
30
40
50
60
70
80
90
100
120
450
455
460
465
470
475

(a) (b) (c) (d) (e)

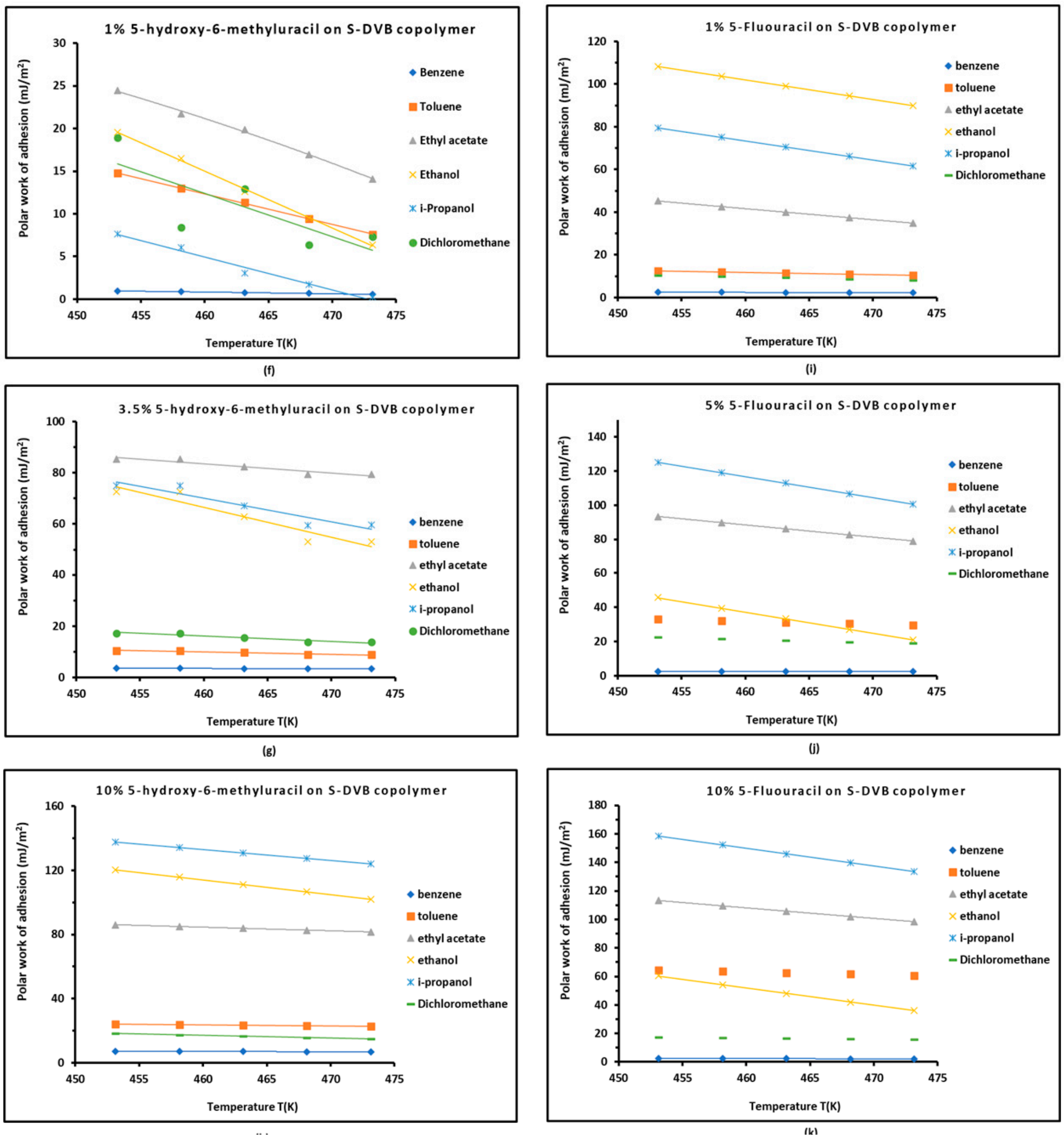


Figure 3. Variations of the polar component of the work of adhesion $W_a^{\mathrm{p}}(T)$ of solvents on the modified S-DVB copolymer versus the temperature at different modifier percentages. S-DVB copolymer (a), 1% Melamine/S-DVB (b), 2% Melamine/S-DVB (c), 3% Melamine/S-DVB (d), 4% Melamine/S-DVB (e), 1% 5-HMU/S-DVB (f), 3.5% 5-HMU/S-DVB (g), 10% 5-HMU/S-DVB (h), 1% 5-FU/S-DVB (i), 5% 5-FU/S-DVB (j), and 10% 5-FU/S-DVB (k).

The sum of the two dispersive and polar contributions of the adhesion work allowed the determination of the total work of adhesion of the various solvents on the different modified copolymers. The obtained results were given in Table 4 in the form of the equations $W_a(T)$ functions of temperature, the modifier and its percentage. Two new thermodynamic parameters were defined. The first one is the surface entropy ΔS_S of adhesion work and the second term is relative to the surface enthalpy ΔH_S of adhesion work. The general equation of $W_a(T)$ can be then written as:

$$W_a(T) = \Delta H_S - T\Delta S_S \qquad (14)$$

Table 4. Equations of total work of adhesion $W_a(T)$ (in mJ/m^2) of the various model organic solvents on S-DVB modified by melamine, 5-HMU, and 5-FU at by different percentages, with the linear regression coefficients, the surface entropy ΔS_S (in mJ m^{-2} K^{-1}) and the surface enthalpy ΔH_S (in mJ m^{-2}) of adhesion work, the maximum temperature $T_{Max} = \Delta H_S/\Delta S_S$.

S-DVB Copolymer

Solvents	$\boldsymbol{W_a(T)}$	$\boldsymbol{\Delta S_S}$	$\boldsymbol{\Delta H_S}$	$\boldsymbol{T_{Max.}}$(K)	R²
n-hexane	$W_a(T)$ = -1.07 T + 513.05	1.07	513.05	477.57	0.9972
n-heptane	$W_a(T)$ = -0.92 T + 454.45	0.92	454.45	495.64	0.9858
n-octane	$W_a(T)$ = -0.95 T + 475.17	0.95	475.17	502.61	0.9804
n-nonane	$W_a(T)$ = -0.99 T + 498.93	0.99	498.93	506.17	0.9778
Benzene	$W_a(T)$ = -1.10 T + 550.93	1.10	550.93	502.67	0.9812
Toluene	$W_a(T)$ = -1.29 T + 664.32	1.29	664.32	514.42	0.9754
Ethyl acetate	$W_a(T)$ = -1.29 T + 669.43	1.29	669.43	518.38	0.9859
Ethanol	$W_a(T)$ = -1.85 T + 945.32	1.85	945.32	510.21	0.9932
i-Propanol	$W_a(T)$ = -1.74 T + 891.1	1.74	891.1	511.04	0.9905
Dichloromethane	$W_a(T)$ = -1.23 T + 654.39	1.23	654.39	531.03	0.9921

1% Melamine / S-DVB Copolymer

Solvents	$\boldsymbol{W_a(T)}$	$\boldsymbol{\Delta S_S}$	$\boldsymbol{\Delta H_S}$	$\boldsymbol{T_{Max.}}$	R²
n-hexane	$W_a(T)$ = -1.00 T + 480.8	1.00	480.8	479.55	0.9967
n-heptane	$W_a(T)$ = -0.66 T + 335.68	0.65	335.68	512.65	0.9999
n-octane	$W_a(T)$ = -0.59 T + 317.85	0.60	317.85	531.17	0.9999
n-nonane	$W_a(T)$ = -0.58 T + 316.17	0.58	316.17	542.69	0.9999
Benzene	$W_a(T)$ = -0.71 T + 375.92	0.71	375.92	531.94	0.9999
Toluene	$W_a(T)$ = -0.57 T + 335.24	0.57	335.24	585.37	0.9999
Ethyl acetate	$W_a(T)$ = -0.58 T + 319.32	0.58	319.32	554.47	0.9999
Ethanol	$W_a(T)$ = -0.64 T + 368.46	0.64	368.46	574.46	0.9999
i-Propanol	$W_a(T)$ = -1.21 T + 668.61	1.21	668.61	553.39	0.9999

Dichloromethane	$W_a(T) = -1.34\ T + 662.71$	1.34	662.71	494.38	0.9997
2% Melamine / S-DVB Copolymer					
Solvents	$\boldsymbol{W_a(T)}$	ΔS_S	ΔH_S	$T_{Max.}$	R^2
n-hexane	$W_a(T) = -0.78\ T + 372.02$	0.78	372.02	477.93	0.9946
n-heptane	$W_a(T) = -0.52\ T + 265.41$	0.52	265.41	506.89	0.994
n-octane	$W_a(T) = -0.50\ T + 260.01$	0.50	260.01	520.64	0.9894
n-nonane	$W_a(T) = -0.50\ T + 263.73$	0.50	263.73	528.73	0.9864
Benzene	Wa = -0.59 T + 308.05	0.59	308.05	519.30	0.9904
Toluene	$W_a(T) = -0.58\ T + 324.78$	0.58	324.78	563.95	0.9789
Ethyl acetate	$W_a(T) = -0.59\ T + 334.41$	0.59	334.41	568.34	0.9892
Ethanol	$W_a(T) = -1.5\ T + 764.61$	1.50	764.61	510.52	0.9983
i-Propanol	$W_a(T) = -1.15\ T + 694.21$	1.15	694.21	602.30	0.9964
Dichloromethane	$W_a(T) = -0.85\ T + 502.92$	0.85	502.92	590.42	0.9978
3% Melamine / S-DVB Copolymer					
Solvents	$\boldsymbol{W_a(T)}$	ΔS_S	ΔH_S	$T_{Max.}$	R^2
n-hexane	$W_a(T) = -0.88\ T + 423.69$	0.88	423.69	479.34	0.9952
n-heptane	$W_a(T) = -0.60\ T + 307.28$	0.60	307.28	509.75	0.9954
n-octane	$W_a(T) = -0.56\ T + 296.17$	0.56	296.17	525.68	0.9917
n-nonane	$W_a(T) = -0.56\ T + 297.66$	0.56	297.66	535.36	0.9889
Benzene	$W_a(T) = -0.67\ T + 355.5$	0.67	355.5	529.33	0.9926
Toluene	$W_a(T) = -0.65\ T + 363.83$	0.65	363.83	557.68	0.9822
Ethyl acetate	$W_a(T) = -0.69\ T + 392.76$	0.69	392.76	566.75	0.992
Ethanol	$W_a(T) = -2.05\ T + 1049.6$	2.05	1049.6	511.88	0.9991
i-Propanol	$W_a(T) = -1.72\ T + 875.58$	1.72	875.58	510.42	0.9983
Dichloromethane	$W_a(T) = -1.12\ T + 577.52$	1.12	577.52	516.75	0.9985
4% Melamine / S-DVB Copolymer					
Solvents	$\boldsymbol{W_a(T)}$	ΔS_S	ΔH_S	$T_{Max.}$	R^2
n-hexane	$W_a(T) = -0.96\ T + 460.73$	0.96	460.73	479.28	0.9952
n-heptane	$W_a(T) = -0.63\ T + 323.74$	0.63	323.74	511.52	0.9969
n-octane	$W_a(T) = -0.58\ T + 308.83$	0.58	308.83	528.91	0.995
n-nonane	$W_a(T) = -0.57\ T + 308.54$	0.57	308.54	539.59	0.9934
Benzene	$W_a(T) = -0.71\ T + 377.26$	0.71	377.26	535.04	0.9956
Toluene	$W_a(T) = -0.67\ T + 394.99$	0.66	394.99	594.24	0.9896
Ethyl acetate	$W_a(T) = -0.73\ T + 407.05$	0.73	407.05	557.37	0.9956
Ethanol	$W_a(T) = -1.78\ T + 950.98$	1.78	950.98	535.58	0.9993
i-Propanol	$W_a(T) = -1.47\ T + 797.06$	1.47	797.06	543.18	0.9986
Dichloromethane	$W_a(T) = -1.17\ T + 638$	1.17	638	545.21	0.9988
1% 5-HMU / S-DVB Copolymer					
Solvents	$\boldsymbol{W_a(T)}$	ΔS_S	ΔH_S	$T_{Max.}$	R^2
n-hexane	$W_a(T) = -0.79\ T + 377.09$	0.79	377.09	478.42	0.9996
n-heptane	$W_a(T) = -0.59\ T + 297.17$	0.59	297.17	503.00	0.9969
n-octane	$W_a(T) = -0.58\ T + 298.07$	0.58	298.07	514.00	0.9949

n-nonane	$W_a(T)$ = -0.59 T + 306.26	0.59	306.26	520.14	0.9939
Benzene	$W_a(T)$ = -0.69 T + 355.57	0.69	355.57	512.20	0.9956
Toluene	$W_a(T)$ = -1.01 T + 530.27	1.01	530.27	523.16	0.9969
Ethyl acetate	$W_a(T)$ = -1.08 T + 552.6	1.08	552.6	514.14	0.9991
Ethanol	$W_a(T)$ = -1.23 T + 617.99	1.23	617.99	501.37	0.9969
i-Propanol	$W_a(T)$ = -0.98 T + 495.06	0.98	495.06	507.75	0.9897
Dichloromethane	$W_a(T)$ = -1.26 T + 619.03	1.26	619.03	490.52	0.9023
3.5% 5-HMU / S-DVB Copolymer					
Solvents	$W_a(T)$	ΔS_S	ΔH_S	$T_{Max.}$	R²
n-hexane	$W_a(T)$= -0.80 T + 380.26	0.80	380.26	477.77	0.999
n-heptane	$W_a(T)$ = -0.66 T + 326.22	0.66	326.22	497.51	0.997
n-octane	$W_a(T)$ = -0.67 T + 337.84	0.67	337.84	505.37	0.9958
n-nonane	$W_a(T)$ = -0.69 T + 353	0.69	353	509.53	0.9954
Benzene	$W_a(T)$ = -0.78 T + 397.1	0.78	397.1	508.39	0.996
Toluene	$W_a(T)$ = -0.89 T + 471.28	0.89	471.28	526.98	0.9955
Ethyl acetate	$W_a(T)$ = -0.97 T + 567.37	0.97	567.37	582.46	0.9976
Ethanol	$W_a(T)$ = -1.66 T + 862.63	1.66	862.63	520.85	0.9992
i-Propanol	$W_a(T)$ = -1.49 T + 795.55	1.490	795.55	533.78	0.9988
Dichloromethane	$W_a(T)$ = -0.99 T + 495.17	0.986	495.17	502.00	0.9989
10% 5-hydroxy-6-methyluracil / S-DVB Copolymer					
Solvents	$W_a(T)$	ΔS_S	ΔH_S	$T_{Max.}$	R²
n-hexane	$W_a(T)$ = -0.76 T + 361.98	0.76	361.98	476.48	0.9998
n-heptane	$W_a(T)$ = -0.70 T + 344.16	0.70	344.16	490.89	0.9996
n-octane	$W_a(T)$ = -0.75 T + 371.62	0.75	371.62	495.49	0.9993
n-nonane	$W_a(T)$ = -0.80 T + 396.43	0.80	396.43	497.78	0.9991
Benzene	$W_a(T)$ = -0.87 T + 438.65	0.87	438.65	502.58	0.9994
Toluene	$W_a(T)$ = -1.08 T + 562.98	1.08	562.98	522.63	0.9979
Ethyl acetate	$W_a(T)$ = -1.02 T + 585.03	1.02	585.03	573.90	0.9992
Ethanol	$W_a(T)$ = -1.71 T + 931.89	1.71	931.89	544.61	0.9998
i-Propanol	$W_a(T)$ = -1.54 T + 878.5	1.54	878.5	569.09	0.9995
Dichloromethane	$W_a(T)$ = -1.01 T + 503.78	1.01	503.78	499.09	0.9998
1% 5-Flouuracil / S-DVB Copolymer					
Solvents	$W_a(T)$	ΔS_S	ΔH_S	$T_{Max.}$	R²
n-hexane	$W_a(T)$ = -0.85 T + 409.22	0.85	409.22	480.47	0.9991
n-heptane	$W_a(T)$ = -0.53 T + 276.42	0.53	276.42	517.25	0.9892
n-octane	$W_a(T)$ = -0.47 T + 253.35	0.47	253.35	540.65	0.9742
n-nonane	$W_a(T)$ = -0.44 T + 247.09	0.44	247.09	556.26	0.9622
Benzene	$W_a(T)$ = -0.56 T + 301.56	0.56	301.56	540.91	0.9769
Toluene	$W_a(T)$ = -0.48 T + 295.44	0.48	295.44	614.09	0.9325
Ethyl acetate	$W_a(T)$ = -0.92 T + 507.43	0.92	507.43	554.51	0.9892
Ethanol	$W_a(T)$ = -1.32 T + 753.74	1.32	753.74	569.94	0.9949
i-Propanol	$W_a(T)$ = -1.29 T + 716.03	1.29	716.03	556.01	0.9931
Dichloromethane	$W_a(T)$ = -0.85 T + 432.53	0.85	432.53	508.32	0.997

5% 5-Fluouracil / S-DVB Copolymer

Solvents	$\boldsymbol{W_a(T)}$	$\boldsymbol{\Delta S_S}$	$\boldsymbol{\Delta H_S}$	$\boldsymbol{T_{Max.}}$	R^2
n-hexane	$W_a(T) = -0.91\ T + 438.27$	0.91	438.27	479.61	0.9983
n-heptane	$W_a(T) = -0.60\ T + 309.29$	0.60	309.29	512.15	0.9978
n-octane	$W_a(T) = -0.55\ T + 293.5$	0.55	293.5	530.26	0.9956
n-nonane	$W_a(T) = -0.54\ T + 292.32$	0.54	292.32	541.53	0.9941
Benzene	$W_a(T) = -0.6554\ T + 347.96$	0.6554	347.96	530.91	0.9961
Toluene	$W_a(T) = -0.6949\ T + 415.71$	0.6949	415.71	598.23	0.9927
Ethyl acetate	$W_a(T) = -1.2143\ T + 693.27$	1.2143	693.27	570.92	0.9986
Ethanol	$W_a(T) = -1.7361\ T + 880.53$	1.7361	880.53	507.19	0.9993
i-Propanol	$W_a(T) = -1.7287\ T + 963.71$	1.7287	963.71	557.48	0.9991
Dichloromethane	$W_a(T) = -0.9861\ T + 507.27$	0.9861	507.27	514.42	0.9991

10% 5-Fluouracil / S-DVB Copolymer

Solvents	$\boldsymbol{W_a(T)}$	$\boldsymbol{\Delta S_S}$	$\boldsymbol{\Delta H_S}$	$\boldsymbol{T_{Max.}}$	R^2
n-hexane	$W_a(T) = -0.94\ T + 451.85$	0.94	451.85	479.67	0.9976
n-heptane	$W_a(T) = -0.64\ T + 327.09$	0.64	327.09	510.76	0.9992
n-octane	$W_a(T) = -0.59\ T + 313.4$	0.59	313.4	527.52	0.9986
n-nonane	$W_a(T) = -0.58\ T + 313.9$	0.58	313.9	537.68	0.9981
Benzene	$W_a(T) = -0.70\ T + 369.84$	0.70	369.84	528.04	0.9987
Toluene	$W_a(T) = -0.77\ T + 484.8$	0.77	484.8	627.41	0.9978
Ethyl acetate	$W_a(T) = -1.28\ T + 744.91$	1.28	744.91	581.55	0.9996
Ethanol	$W_a(T) = -1.77T + 912.74$	1.77	912.74	515.38	0.9998
i-Propanol	$W_a(T) = -1.80\ T + 1031.2$	1.80	1031.2	572.89	0.9997
Dichloromethane	$W_a(T) = -0.93\ T + 478.52$	0.93	478.52	514.04	0.9993

The values of ΔH_S and ΔS_S of the different organic solvents given in Table 4 for the modified copolymers at different modifier percentages led to linear relations between these surface parameters and the corresponding percentage (q) of melamine (noted Mela), 5-HMU, and 5-FU. The equations of $\Delta H_S(q)$ and $\Delta S_S(q)$ relative to the work of adhesion on the modified copolymers were given in Table 5 with the linear regression coefficients. The results in Table 5 led to the following general equations:

$$\Delta H_S(q) = aq + b \qquad (15)$$

$$\Delta S_S(q) = cq + d \qquad (16)$$

Where a, b, c, and d given in Table 5 are constant coefficients depending on the work of adhesion of the solvents on the modified S-DVB.

Table 5. Equations of the surface adhesion parameters $\Delta H_S(q)$ and $\Delta S_S(q)$ of the different solvents on the modified copolymers as a function of the modifier percentage with the linear regression coefficients.

S-DVB Copolymer				
Solvents	**Equation** $\Delta \boldsymbol{S_S(q)}$ (in mJ $m^{-2}K^{-1}$)	**R²**	**Equation** $\Delta \boldsymbol{H_S(q)}$ (in mJ m^{-2})	**R²**
n-hexane	ΔS_S = 0.076 q (Mela) + 0.65	0.9757	ΔH_S = 46.92 q (Mela) + 277.19	0.9948
n-heptane	ΔS_S = 0.033 q (Mela) + 0.615	0.9945	ΔH_S = 33.70 q (Mela) + 196.20	0.9699
n-octane	ΔS_S = 0.024 q (Mela) + 0.485	0.9931	ΔH_S = 24.44 q (Mela) + 215.01	0.9701
n-nonane	ΔS_S = 0.016 q (Mela) + 0.51	0.9143	ΔH_S = 22.05 q (Mela) + 223.96	0.9647
Benzene	ΔS_S = 0.065 q (Mela) + 0.46	0.9837	ΔH_S = 34.78 q (Mela) + 242.54	0.9821
Toluene	ΔS_S = 0.031 q (Mela) + 0.545	0.9468	ΔH_S = 30.83 q (Mela) + 270.14	0.9852
Ethyl acetate	ΔS_S = 0.055 q (Mela) + 0.51	0.9181	ΔH_S = 32.15 q (Mela) + 283.00	0.9313
Ethanol	ΔS_S = 0.235 q (Mela) + 0.97	0.9612	ΔH_S = 193.26 q (Mela) + 225.28	0.9515
i-Propanol	ΔS_S = 0.146 q (Mela) + 1.04	0.9769	ΔH_S = 101.67 q (Mela) + 517.19	0.9238
Dichloromethane	ΔS_S = -0.09 q (Mela) + 1.41	0.962	ΔH_S = 60.23 q (Mela) + 394.56	0.9885
S-DVB/5-HMU				
Solvents	**Equation** $\Delta \boldsymbol{S_S(q)}$ (in mJ $m^{-2}K^{-1}$)	**R²**	**Equation** $\Delta \boldsymbol{H_S(q)}$ (in mJ m^{-2})	**R²**
n-hexane	ΔS_S = -0.003 q (5-HMU) + 0.793	0.9963	ΔH_S = 1.15 q (5-HMU) + 376.06	0.9992
n-heptane	ΔS_S = 0.011 q (5-HMU) + 0.592	0.9106	ΔH_S = 3.98 q (5-HMU) + 306.11	0.9177
n-octane	ΔS_S = 0.018 q (5-HMU) + 0.582	0.9209	ΔH_S = 7.58 q (5-HMU) + 299.23	0.9137
n-nonane	ΔS_S = 0.022 q (5-HMU) + 0.589	0.9508	ΔH_S = 9.35 q (5-HMU) + 306.71	0.9276
Benzene	ΔS_S = 0.019 q (5-HMU) + 0.689	0.9382	ΔH_S = 8.66 q (5-HMU) + 355.24	0.9383
Toluene	ΔS_S = 0.02 q (5-HMU) + 0.88	0.9999	ΔH_S = 3.55 q (5-HMU) + 527.96	0.9914
Ethyl acetate	ΔS_S = -0.006 q (5-HMU) + 1.080	0.9382	ΔH_S = 3.43 q (5-HMU) + 551.78	0.9606
Ethanol	ΔS_S = 0.050 q (5-HMU) + 1.233	0.9261	ΔH_S = 33.10 q (5-HMU) + 610.84	0.9582
i-Propanol	ΔS_S = 0.033 q (5-HMU) + 1.205	0.9999	ΔH_S = 39.70 q (5-HMU) + 497.81	0.9249
Dichloromethane	ΔS_S = -0.026 q (5-HMU) + 1.254	0.9008	ΔH_S = -12.08 q (5-HMU) + 620.49	0.9479
S-DVB/5-FU				
Solvents	**Equation** $\Delta \boldsymbol{S_S(q)}$ (in mJ $m^{-2}K^{-1}$)	**R²**	**Equation** $\Delta \boldsymbol{H_S(q)}$ (in mJ m^{-2})	**R²**
n-hexane	ΔS_S = 0.010 q (5-FU) + 0.848	0.9368	ΔH_S = 4.65 q (5-FU) + 408.29	0.9286
n-heptane	ΔS_S = 0.012 q (5-FU) + 0.526	0.9523	ΔH_S = 5.55 q (5-FU) + 274.69	0.9462
n-octane	ΔS_S = 0.013 q (5-FU) + 0.467	0.9368	ΔH_S = 6.56 q (5-FU) + 251.75	0.9357
n-nonane	ΔS_S = 0.015 q (5-FU) + 0.439	0.9089	ΔH_S = 7.30 q (5-FU) + 245.52	0.9311
Benzene	ΔS_S = 0.015 q (5-FU) + 0.557	0.9286	ΔH_S = 7.46 q (5-FU) + 300.03	0.9296
Toluene	ΔS_S = 0.032 q (5-FU) + 0.478	0.9026	ΔH_S = 20.74 q (5-FU) + 288.02	0.9529
Ethyl acetate	ΔS_S = 0.026 q (5-FU) + 1.037	0.9126	ΔH_S = 25.73 q (5-FU) + 511.32	0.8628
Ethanol	ΔS_S = 0.049 q (5-FU) + 1.312	0.9243	ΔH_S = 11.00 q (5-FU) + 809.76	0.9292
i-Propanol	ΔS_S = 0.056 q (5-FU) + 1.284	0.9141	ΔH_S = 23.48 q (5-FU) + 811.75	0.9257
Dichloromethane	ΔS_S = 0.019 q (5-FU) + 0.892	0.9999	ΔH_S = 5.08 q (5-FU) + 428.94	0.9898

The combination of Equations (14) to (16) led to a universal equation giving the work of adhesion $W_a(T,q)$ of organic solvent on a copolymer modified by a modifier percentage q:

$$\boldsymbol{W_a(T,q)} = a\boldsymbol{q} + b - \boldsymbol{T}(c\boldsymbol{q} + d) \qquad (17)$$

$W_a(T,q)$ given by Equation (17) is a function of two variables T and q.

The above equation represents a quantification of the work of adhesion knowing the temperature and the modifier percentage. This result is similar to that obtained in previous studies during the study of the adsorption of PMMA on silica and alumina at different recovery fractions where the polar free energy of adsorption was correlated to the two thermodynamic variables such as the temperature and the percentage of adsorption.

Another interesting result was obtained from Table 5 by drawing the variations of ΔH_S and ΔS_S of the different modified copolymers. Linear relation of the surface enthalpy of adhesion work $\Delta H_S(\Delta S_S)$ was obtained versus the surface entropy for the different copolymers and a new surface temperature T_S was defined. This new variable constitutes a real characteristic of the copolymer. The linear equations were given in table 6.

Table 6. Equations of ΔH_S as a function of $\Delta S_S$of the different modified copolymers with the values of T_S and the corresponding linear regression coefficients.

Copolymer	**Equations** $\boldsymbol{\Delta H_S = f(\Delta S_S)}$	$\boldsymbol{T_S}$	**R²**
S-DVB Copolymer	ΔH_S = 527.12 ΔS_S - 23.502	527.12	0.9923
1% Melamine / S-DVB Copolymer	ΔH_S = 476.71 ΔS_S + 42.251	476.71	0.9672
2% Melamine / S-DVB Copolymer	ΔH_S = 543.47 ΔS_S - 1.841	543.47	0.9596
3% Melamine / S-DVB Copolymer	ΔH_S = 500.3 ΔS_S + 18.342	500.3	0.9957
4% Melamine / S-DVB Copolymer	ΔH_S = 532.74 ΔS_S + 1.972	532.74	0.9882
1% 5-HMU / S-DVB Copolymer	ΔH_S = 494.38 ΔS_S + 9.860	494.38	0.9917
3.5% 5-HMU / S-DVB Copolymer	ΔH_S = 546.19 ΔS_S - 25.452	546.19	0.9838
10% 5-HMU / S-DVB Copolymer	ΔH_S = 609.06 ΔS_S - 86.224	609.06	0.9884
1% 5-Fluouracil / S-DVB Copolymer	ΔH_S = 558.33 ΔS_S - 11.407	558.33	0.9793
5% 5-Fluouracil / S-DVB Copolymer	ΔH_S = 534.46 ΔS_S - 0.318	534.46	0.9803
10% 5-Fluouracil / S-DVB Copolymer	ΔH_S = 556.11 ΔS_S - 14.185	556.11	0.973

The various equations presented in Table 6 can be generally described by the following equation for all materials:

$$\boldsymbol{\Delta H_S = \alpha\, \Delta S_S + \beta} \tag{18}$$

where the slope $\boldsymbol{\alpha}$ represents an isokinetic surface temperature T_S ($T_S = \boldsymbol{\alpha}$) at which all processes in series of organic solvents proceed with the same work of adhesion here given by the constant parameter $\boldsymbol{\beta}$. This interesting equation traduces the surface enthalpy – surface entropy compensation with excellent linear regression coefficient for all studied copolymers.

4. Conclusions

A new method was proposed to determine the variations of the work of adhesion $W_a(T)$ of model organic solvents on S-DVB copolymer modified by melamine, 5-HMU, and 5-FU at different percentages by varying the temperature. The surface properties of modified copolymers such as the dispersive and polar free energy of adsorption, the London dispersive and polar surface energies of copolymers were used to determine the dispersive $W_a^{\mathrm{d}}(T)$ and polar $W_a^{\mathrm{p}}(T)$ works of adhesion of the various organic model solvents on S-DVB copolymer as a function of temperature and modifier percentage. Results showed an excellent linearity of $W_a^{\mathrm{d}}(T)$ and $W_a^{\mathrm{p}}(T)$ as a function of temperature for all solvents and copolymers with a decrease against the temperature depending on the modifier nature and its percentage. The highest polar adhesion work was obtained with ethanol on S-DVB modified by melamine while the values of $W_a^{\mathrm{p}}(T)$ of benzene and toluene were the lowest. The comparison between the various modifiers led to conclude that the maximum of adhesion work was obtained with 5-FU on S-DVB copolymer. The work of adhesion was correlated to the surface enthalpy ΔH_S and entropy ΔS_S of organic solvents adsorbed on copolymers at different modifier percentages (q) via the following equation:

$$W_a(T,q) = \Delta H_S(q) - T\Delta S_S(q)$$

It was proved that $\Delta H_S(q)$ and $\Delta S_S(q)$ linearly varied as a function of the modifier percentage (q) as follows: The results in Table 5 led to the following general equations:

$$\Delta H_S(q) = aq + b$$

$$\Delta S_S(q) = cq + d$$

A new relation of the work of adhesion $W_a(T,q)$ function of the two variables T and q was therefore proposed:

$$W_a(T,q) = aq + b - T(cq + d)$$

Furthermore, linear relations of the surface enthalpy of adhesion work ΔH_S as a function of the surface entropy of adhesion were obtained and a new surface temperature T_S representing an isokinetic surface temperature was defined.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Figure S1. Variations of the polar surface energy $\gamma_l^{\mathrm{p}}(T)$ of solvents as a function of temperature for S-DVB copolymer at different modifier percentages. S-DVB copolymer (a), 1% Melamine/S-DVB (b), 2% Melamine/S-DVB (c), 3% Melamine/S-DVB (d), 4% Melamine/S-DVB (e), 1% 5-HMU/S-DVB (f), 3.5% 5-HMU/S-DVB (g), 10% 5-HMU/S-DVB (h), 1% 5-FU/S-DVB (i), 5% 5-FU/S-DVB (j), and 10% 5-FU/S-DVB (k). Figure S2. Variations of the dispersive component of the work of adhesion $W_a^{\mathrm{d}}(T)$ of solvents on the modified S-DVB copolymer versus the temperature at different modifier percentages. S-DVB copolymer (a), 1% Melamine/S-DVB (b), 2% Melamine/S-DVB (c), 3% Melamine/S-DVB (d), 4% Melamine/S-DVB (e), 1% 5-HMU/S-DVB (f), 3.5% 5-HMU/S-DVB (g), 10% 5-HMU/S-DVB (h), 1% 5-FU/S-DVB (i), 5% 5-FU/S-DVB (j), and 10% 5-FU/S-DVB (k).

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