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THE INFLUENCE OF MICROSTRUCTURE OF POLYMER CHAIN ON ADHESIVE PROPERTIES OF POLY(V(STYRENEN-BUTYL ACRYLATE)) BINARY COPOLYMER FILMS FORMED FROM VARIOUS SOLVENTS

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ABSTRACT
The surface properties of the films of poly(styrene/butyl acrylate) binary copolymers (PS/PNBA) with 30% styrene (ST) mole fraction and various monomer unit distribution (random and gradient), formed from various solvents (toluene, acetone) were studied. The original approach for investigation of the influence of the chain microstructure and solvent thermodynamic quality on the energy characteristics of the surface of the copolymer films and their adhesive properties with respect to solid substrates of various polarity (glass, steel, polyethylene and polyethylene terephthalate) was developed [1]. This approach is based on the combination of contact angle measurements, ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared), quantum chemical calculations of polymer–solvent interactions and strength tests. The sensitivity of adhesive characteristics to solvent nature of the films of the gradient copolymers differed from the same characteristics of random copolymers. The results obtained demonstrated the principle possibility of regulation of the copolymer adhesion by varying chain architecture and nature of the solvent from which the copolymer films were formed.

INTRODUCTION
The gentle regulation of polymer adhesion is one of the actual problems of modern material science. The insertion of second monomer in polymer chain is one of the common synthetic approaches for the realization of this goal. But it should be noted that the development of principles of polymer

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design is currently outpacing the understanding of regularities of influence on the polymer adhesive properties such parameters as polymer chain microstructure and thermodynamic quality of solvent, from which polymer films were formed. The aim of our study was the development of experimental methodology with respect to study of adhesion of binary copolymers to various solid substrates using the combination of contact angle measurements and other techniques, namely – with ATR-FTIR, quantum chemical simulation and strength tests.

EXPERIMENTAL
The objects of our study were films of PS/PNBA with gradient (GC-30) and random (RC-30) monomer distribution (Fig.1). These copolymers were synthesized via controlled radical polymerization via the reversible addition-fragmentation chain-transfer mechanism (RAFT polymerization) using dibenzyl trithiocarbonate as chain transfer agent [1]. The characteristics of copolymers were: $M_n = 51$ kDa, $M_w/M_n = 1.11$ for GC-30 and $M_n = 58.7$ kDa, $M_w/M_n = 1.56$ for RC-30.

Figure 1. Scheme of order of sequence of monomer units in PS/PNBA chains with random (RC) and gradient (GC) microstructure: ○ butyl acrylate, ● styrene, △ trithiocarbonate group.

The polymer films were formed from toluene (thermodynamically «good» solvent for ST and «bad» for NBA) and acetone («good» for n-butyl acrylate (NBA) and «bad» for ST. The alumina plates were used as a solid carriers. In our previous study the interrelation between PS/PNBA chain microstructure, solvent nature and surface energy characteristics of polymer films was illustrated; the styrene mole fractions were 10 and 60% [1]. In this study the ST mole fraction was 30% in order to allow the formation of adhesion compounds and, on the other hand, to provide the relatively high glass temperatures to avoid the impropriety of strength tests caused by the high fluidity of polymer adhesive.

The sessile drop technique was applied for contact angle measurements. The surface energy of polymer films ($\gamma_{SV}$), its polar ($\gamma_{PV}$) and dispersive ($\gamma_{SV}$) components were calculated using experimental contact angles of the drops of probe liquids (water and diiodomethane) in accordance with Owens-
Wendt-Kaelble approach [2]. The methods of calculation of the work of adhesion of PS/PNBA to water, simulating the polar solid substrate (Wpp) and octane, simulating the nonpolar one (Wdd) as well as technique of ATR-F11R study are presented in details in [1].

The quantum chemical simulation of interaction of the NBA and ST with acetone or toluene was performed by semi-empirical method AM-1 with MOPAC software package.

The strength tests were performed at the breaking machine Zwick/Roell Z010. The destruction of the adhesive compounds of PS/PNBA with solid substrates was performed by exfoliation technique (peel angle 180°) with subsequent identification of exfoliation mechanism using scanning electronic microscope Philips SEM-500. The solid substrates were glass, steel, polyethylene and polyethylene terephthalate (PET). The PS/PNBA layer thickness was 50μm. All measurements were carried out at 20°C.

RESULTS AND DISCUSSION

The γSV of PS/PNBA brings a dominant contribution in the surface energy value for all copolymer films, independently of the solvent nature from which polymer film was formed (Table 1). Thus, the close values of Wdd and dispersive (γSV) modes and the work of adhesion of PS/PNBA to polar (Wpp) and nonpolar (Wdd) liquid, simulating solid substrates.

<table>
<thead>
<tr>
<th>polymer</th>
<th>solvent</th>
<th>γSV, mJ/m²</th>
<th>γSV, mJ/m²</th>
<th>γSV, mJ/m²</th>
<th>Wdd, mJ/m²</th>
<th>Wpp, mJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-30</td>
<td>toluene</td>
<td>44</td>
<td>44</td>
<td>-</td>
<td>61</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>acetone</td>
<td>45</td>
<td>43</td>
<td>2</td>
<td>61</td>
<td>106</td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>42</td>
<td>41</td>
<td>1</td>
<td>60</td>
<td>96</td>
</tr>
<tr>
<td>RC-30</td>
<td>acetone</td>
<td>41</td>
<td>40</td>
<td>1</td>
<td>59</td>
<td>101</td>
</tr>
</tbody>
</table>

for all copolymer films are rather expectable.

In comparison to γSV, the γSV values are negligibly low. Nevertheless, a difference between the Wpp for PS/PNBA of different microstructure with respect to solvent nature was found. The noticeable difference between Wpp is observed in case of GC-30. The strength of adhesive compounds (A) of GC-30 with different substrates also differs considerably for polyethylene and other polar substrates, for example, PET (Fig. 2).

In case of RC-30 the relationship between A and Wpp could not be established due to the cohesion destruction of adhesive compounds. The adhesion of PS/PNBA to polar phases is realized due to NBA comonomer, containing the polar groups. Thus, the result obtained may be
caused by the higher mobility of NBA monomer units in polymer chain with gradient microstructure in comparison to random one.

\[ A, \text{ mN m}^{-1} \]
\[ V, \text{ mm min}^{-1} \]

**Polyethylene**

\[ \bullet \quad 2 \]
\[ \circ \quad 1 \]

\[ \bullet \quad 2 \]
\[ \circ \quad 1 \]

**Polyethylene Terephthalate**

\[ \bullet \quad 2 \]
\[ \circ \quad 1 \]

\[ \bullet \quad 2 \]
\[ \circ \quad 1 \]

Figure 2. Plot peel strength \((A)\) versus delaminating speed \((V)\) for adhesive compounds of RC-30 films, formed from toluene (1) and acetone (2) on solid substrates.

Indeed, quantum chemical calculations proved the energetic benefit of reorientation of NBA units contacting with polar phase (water). For example, in the case of triad of NBA units (highly probable in case of GC-30) the energy of intermolecular interaction \(\Delta E = -10\ \text{kJ mol}^{-1}\) is lower in comparison to NBA-water interaction \(\Delta E = -20.8\ \text{kJ mol}^{-1}\).

**CONCLUSIONS**

The new methodological approach to study of influence of chain microstructure and solvent nature on adhesion of polymer films [3] was developed for the new objects. The distinction between the adhesive properties of copolymer films with gradient distribution of monomer units with respect to polar and nonpolar solid substrates formed from different solvents was confirmed by using contact angle measurements, quantum chemical calculations and the strength tests.

**Acknowledgement**

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**REFERENCES**
