# Adhesion of Acrylate-Based Water Dispersion to Polypropylene Hybrid Fabrics

Igor Novák\*, Marek Stach

Polymer Institute of the Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republik

Summary: The increase in the content of crosslinking agent and surfactant in acrylate-based water dispersion results in an increase of surface parameters e.g. total SFE and its polar component, interfacial and mechanical work of adhesion of polyacrylate to PP hybrid fabrics. UV irradiation of polyacrylate coating in the course of accelerating ageing has the same effect on surface and adhesive properties as a crosslinking agent or surfactant and leads to a considerable growth of the total SFE, its polar component, interfacial and mechanical work of adhesion. The increase in the interfacial and mechanical work of adhesion with the increase of the crosslinking agent and/or surfactant content in acrylate-based water dispersion is higher for PES/PP fabrics compared to the PA/PP system. The adhesive properties of the film obtained from acrylate-based water dispersion are substantially influenced by the presence of a surfactant and a crosslinking agent.

### Introduction

Adhesives based on acrylic water dispersion are used in a wide range of bonding applications because of their versatility of adhesive properties, good performance at low temperature performance, water resistance, good thermal stability and low toxicity. [1-3] Also when supplied in a form of polymeric emulsion, flammability and toxicity of the solvents is not an issue. In the application of polymeric water acrylate-based dispersions in paint, paper, textile industry, adhesive, coating, one of the most important properties of these systems is adhesion onto a support. [4,5] A sufficient strength of the adhesion joint on the polyacrylate - fabric interface is an important requirement for application of these systems. From the point of view of adhesion the polymeric film made from water dispersion is specific to certain extent. This film retains from a certain extent the memory of the polymeric particles resulting in shrinking of the film after dessication. Further properties of this film are influenced by content and the nature of the surfactants being usually incompatible with the polymer. It tends to segregate from the film and to accumulate on the interface. [6] The adhesion of acrylate-based dispersion to the fabric is influenced by the composition of the dispersion especially regarding to the presence of various additives.

In this contribution the effect of surfactant and crosslinking agent content on adhesive properties of acrylates-based dispersion to polypropylene hybrid fabrics has been investigated. The effect of UV irradiation of polyacrylate on its adhesion to polypropylene hybrid fabrics was also studied.

# **Experimental Part**

### Materials

The hybrid fabrics polyester/polypropylene (PES/PP), weight ratio 66:34 and polyamide/polypropylene (PA/PP), weight ratio 70:30 (Maytex, Slovak Republic), water acrylate-based dispersion Sokrat 4924 with the properties: pH = 6.0 - 8.5, MFT = 1 °C,  $T_g = -16$  °C and viscosity (Brookfield method) is 750 mPa.s (Chemické závody Sokolov, Czech Republic), melamine - formaldehyde resin as a crosslinking agent (Luební závody Kolín, Czech Republic), dodecyl sulfate, sodium salt as a surfactant (Aldrich, USA).

### Chemicals

Testing liquids for contact angle measurements: ethylene glycol, ethyl ester of 2-aminobenzoic acid, formamide, methylene iodide, glycerin (Merck, Germany), thiodiglycol (Serva, Germany), redistilled water. Methylene chloride (BDH, United Kingdom), aniline, benzyl alcohol, tricrezyl phosphate (Fluka, Switzerland) was used for cleaning the surfaces All chemicals were used as received.

## Surface free energy (SFE) of polymers

The contact angles of polymers were determined by measuring the contact angles using a goniometric microscope Amplival Pol d. The drops of testing liquid were placed onto the polymer surface in a test cell (sessile drop method). Each measurement with a set of testing liquids was repeated five times at RT and the dependencies  $\theta = f(t)$  were extrapolated to t = 0. The polar and dispersive component of the SFE of polymer were calculated by relation<sup>[7]</sup>:

$$\frac{(1+\cos\theta).(\gamma_{LV}^{d}+\gamma_{LV}^{p})}{2} = (\gamma_{LV}^{d}.\gamma_{s}^{d})^{1/2} + (\gamma_{LV}^{p}.\gamma_{s}^{p})^{1/2}$$
(1)

where

 $\theta$  is the contact angle (°),  $\gamma_{LV}^{d}$ ,  $\gamma_{LV}^{p}$  is the polar and dispersive component of the SFE of

testing liquid calculated from  $\gamma_{LV}$ , that is measured using a tensiometer, and tabulated dispersive portion of testing liquid (mJ.m<sup>-2</sup>),

while

$$\gamma_s = \gamma_s^p + \gamma_s^d \tag{2}$$

where

 $\gamma_s$  is the total SFE,  $\gamma_s^p$ ,  $\gamma_s^d$  is the polar and dispersive component of the SFE of polymer (mJ.m<sup>-2</sup>).

## Interfacial work of adhesion

The interfacial work of adhesion was calculated from the values of polar and dispersive components of SFE according to the relation:

$$W_{a_{1,2}} = \frac{4 \cdot (\gamma_1^d + \gamma_2^d)}{\gamma_1^d + \gamma_2^d} + \frac{4 \cdot (\gamma_1^p + \gamma_2^p)}{\gamma_1^p + \gamma_2^p}$$
(3)

where

 $\gamma_1^d, \gamma_2^d$  - dispersive component of SFE of the polymer 1 and 2,

 $\gamma_1^p, \gamma_2^p$  - polar component of SFE of the polymer 1 and 2.

# Mechanical work of adhesion

The mechanical work of adhesion was measured by the 90° peel test of adhesive joint using an aluminum wheel. The adhesive joints were prepared from acrylate-based water dispersion by coating onto the PP hybrid fabrics (PA/PP or PEs/PP) and the technical cotton fabric "Molino" using a coating pad (Dioptra, Turnov). Both fabrics have been fixed together and the adhesive joints have been crosslinked in an oven at 140 °C for 20 minutes. The joints were dried up to a constant weight, then they were cut to strips with dimensions 25 x 200 mm having the testing length 100 mm. Calculation of the mechanical work of adhesion was done according to equation:

$$A_m = \frac{Ps}{b} \tag{4}$$

where

P<sub>s</sub> is the medium stress (N) and b is the width of the adhesive joint (m).

## The preparation of the adhesive system

The adhesive system was prepared in a mixer from acrylate-based water dispersion in a presence of etherified melamine-formaldehyde resin as a crosslinking agent and natrium dodecyl sulphate as a surfactant. After applying onto PP hybrid fabric the crosslinking proceeded in an oven at 140 °C during 20 minutes.

## Accelerating ageing of polyacrylate

The polyacrylate coatings have been irradiated using a 250 W mercury tube. The samples rotated around the mercury tube with a distance 100-mm. Each sample was irradiated by the same dose by such a way.

# **Results and Discussion**

The results are divided into two parts:

- ( i ) surface and adhesive properties of polyacrylate to PP-based fabrics versus concentration of crosslinking agent,
- ( ii ) adhesive properties of polyacrylate after an accelerating ageing using UV irradiation.

The polar component of SFE of polyacrylate in dependence on crosslinking agent amount is given in Fig. 1. Fig. 1 demonstrates the rise of polar component of SFE with an increase of concentration of crosslinking agent. The value of polar component of SFE of polyacrylate also rises with the increase of surfactant content. An addition of surfactant to acrylate-based dispersion results in a decrease of the contact angles and in a growth of the polar component of SFE. The polar component of SFE of polyacrylate increased with the increase of surfactant concentration for system without crosslinking agent from 7.2 mJ.m<sup>-2</sup> (virgin polymer) to 8.1 mJ.m<sup>-2</sup> (for 7 wt.% of surfactant in the system). In the presence of crosslinking agent in the system the polar component of SFE of polyacrylate increased. The polar component of SFE was for polyacrylate initialy higher (up to approximatelly 1 wt.% of crosslinking agent) and subsequently levelled off. An addition of crosslinking agent to the polyacrylate and annealing at higher temperature leads to a formation of a three-dimensional polymer network due to the chemical chemical crosslinking. The addition of surfactant leads to a decrease of contact angles of testing liquids or to an increase in wettability of surface of polyacrylate. The amphiphilic molecules of surfactant are moving by diffusion process to the polymer surface and the SFE of polymer rises.

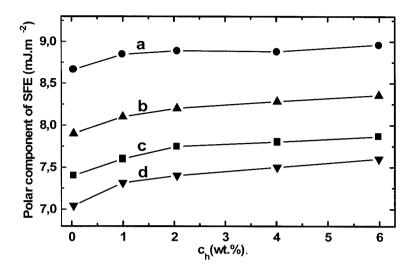


Fig. 1 Polar component of the SFE of polyacrylate as a function of content of crosslinking agent at the surfactant content: a-0 wt.%, b-3 wt.%, c-5 wt.%, d-7 wt.%.

The growth of the polar component of SFE of polyacrylate with an increase of crosslinking agent concentration results in a growth of interfacial work of adhesion to PP-hybrid fabric (Fig. 2). The comparison of the curves a and b in Fig. 2, demonstrates that the interfacial work of adhesion increases in accordance with the growth of hydrophilicity of modified polyacrylate. Thus, adhesive properties of polymer are strongly related to the values of the polar component of SFE by Fig. 1. The increase of the content of crosslinking agent in polyacrylate causes a growth of interfacial work of adhesion. The values of interfacial work of adhesion in the system polyacrylate - PES/PP were higher in comparison with PA/PP system and its increase for PES/PP was from 64 to 69 mJ.m<sup>-2</sup> and for PA/PP from 72.5 to 78.5 mJ.m<sup>-2</sup>.

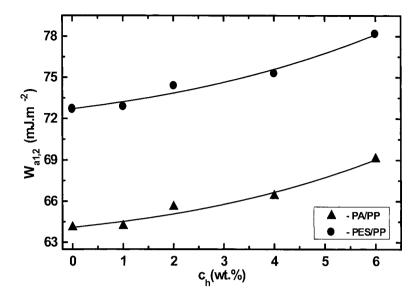


Fig. 2 Interfacial work of adhesion of polyacrylate to PP hybrid fabrics as a function of concentration of crosslinking agent.

The plot of the mechanical work of adhesion of polyacrylate to PP-hybrid fabrics in dependence on the concentration of crosslinking agent is given in Fig. 3. The addition of crosslinking agent to polyacrylate leads to a considerable growth of the mechanical work of adhesion and obtained values were higher for PEs/PP hybrid fabric than for PA/PP material. The mechanical work of adhesion of virgin polyacrylate increased for PES/PP from 250 J.m<sup>-2</sup> to 330 J.m<sup>-2</sup> and for PA/PP from 350 to 440 J.m<sup>-2</sup>, e.g. the increase of mechanical work of adhesion of polyacrylate was in the range 27 – 32 % of the original value (for polyacrylate without crosslinking agent).

The dependence of the total SFE and its polar components in the system polyacrylate – PA/PP as a function of UV irradiation time in the course of accelerated ageing is shown in Fig. 4. It is seen that the surface properties of polyacrylates towards PA/PP rise non-linearly in the course of UV irradiation to a certain limit (5 hours), then the dependence levels off. The more intensive increase in surface properties regarding to total SFE (curve a) was observed for polar component of SFE (curve b), that rises by 34% in comparison with a virgin polymer. Further increase in the (curve a) relative intensity resulted in less pronounced changes of the investigated surface parameter.

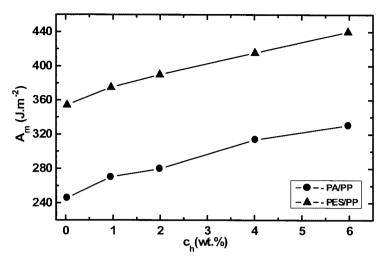


Fig. 3 Mechanical work of adhesion of polyacrylate to PP-based fabrics as a function of concentration of crosslinking agent.

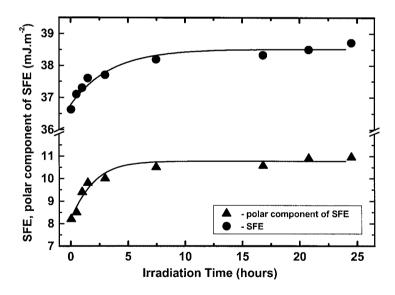


Fig. 4 Surface free energy and its polar component of polyacrylate as a function of UV irradiation time.

This phenomenon can be explained by a summation of factors among whose the mutual deactivation of the radicals formed by UV irradiation at higher radical concentration is supposed to be the most important. The other factors that should be considered are both the decrease of the reaction rate due to diffusion effects and the increase of the concentration of polar sites on the surface of polyacrylate.

The SFE virgin polyacrylate was found to be 36.5 mJ.m<sup>-2</sup>. The SFE of polymer in the course of modification increased and after 24 hours gained the value of 39.0 mJ.m<sup>-2</sup>. The polar component of SFE for UV modified polyacrylate at the same time increased from 8.2 mJ.m<sup>-2</sup> up to 11.2 mJ.m<sup>-2</sup>. The dependence of the surface energy and its polar component on time levels off after about 5-hours.

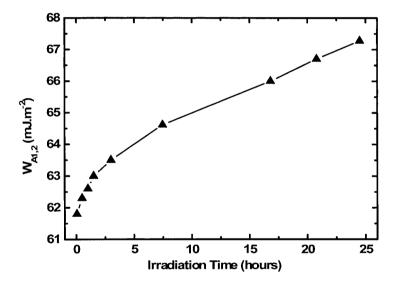


Fig. 5 Interfacial work of adhesion of polyacrylate to PA/PP as a function of UV irradiation time.

Fig. 5 illustrates a non-linear increase of the interfacial work of adhesion for polyacrylate modified by UV to PA/PP in the dependence on the irradiation time. The interfacial work of adhesion for non-modified polymer was equal to 61.8 mJ.m<sup>-2</sup>. The interfacial work of adhesion of investigated system pre-treated by accelerated ageing

increased non-linearly with irradiation time up to the value 67.5 mJ.m<sup>-2</sup> after 24 hours. This value of interfacial work of adhesion reflects the increase in hydrophilicity of polyacrylate in the course of UV pre-treatment.

The increase in crosslinking agent concentration results in the increase of total SFE, interface equilibrium and mechanical work of adhesion of the polyacrylate towards the fabrics. UV irradiation of the polyacrylate leads to an increase of total SFE, its polar component and equilibrium work of adhesion. Comparing the PES/PP and PA/PP, the increase in the equilibrium and mechanical work of adhesion due to the increase in the concentration of hardener and/or surfactant in the polyacrylate dispersion is higher for the latter fabric. The same tendency was observed for the changes caused by UV irradiation.

### Conclusion

It has been shown that the surface and adhesive properties of water- based polyacrylate dispersion depend on the presence of surfactants and a crosslinking agent in the system. The increase of the content of both crosslinking agent and surfactant in the system leads to an increase of the total SFE, interfacial and mechanical work of adhesion of polyacrylate to PP hybrid fabrics. UV irradiation results in a growth of adhesion parameters, e.g. interfacial and mechanical work of adhesion to PA/PP fabric. The interfacial and mechanical work of adhesion of polyacrylate to PP hybrid fabrics was higher in the case of PES/PP fabric as for PA/PP one.

## Acknowledgements

The research was supported by Slovak Grand Agency (VEGA), grant number 2/1060/21.

- [1] A. Kinloch, Adhesion and Adhesives Science and Technology, Chapman and Hall, London 1987, p.24.
- [2] C. Laureau, M. Vincente, M. J. Barandiaran, J. R. Leiza, J. M. Asua, J. Appl. Polym. Sci. 2001, 81, 1258.
- [3] J. Y. Charmeau, E. Kientz, Y. Holl, Progr. Org. Coat. 1996, 27, 87
- [4] I. Novák, I. Chodák, J. Mater. Sci. Let. 1995, 14, 1298.
- [5] P. A. Gerin, Y. Grohens, R. Schirer, Y. Holl, J. Adhes. Sci. Technol. 1999, 13, 217.
- [6] A. H. Beaulieu, F. P. Hoenisch, J. Water Borne Coatings 1987, 10, 3.
- [7] I. Novák, Angew. Makromol. Chem. 1995, 231, 69.