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The Surface Structure and Properties of Films of Latex Blends Based on Vinyl Acetate Copolymer

Vilma ŠIPAILAITĖ-RAMOŠKIENĖ[1*], Kazys Vytautas MICKUS[1], Igoris PROSYČEVAS[2], Asta GUOBIENĖ[2], Viktoras GRIGALIŪNAS[2]

[1]*Faculty of Design and Technologies, Kaunas University of Technology, Studentų 56, LT-3031 Kaunas, Lithuania*
[2]*Institute of Physical Electronics, Kaunas University of Technology, Savanoriu 271, LT-3009 Kaunas, Lithuania*

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The possibility to use water based vinyl acetate / butyl acrylate (VA/BA) copolymer blends with various content of vinyl ester Versatic acid / metyl methacrylate / 2-ethylhexylacrylate / acrylic acid (VeoVa-11/MMA/2-EHA/AA) copolymer for the preparation of adhesive joints have been investigated. The latex film surface structure was studied by atomic force microscopy and scanning electron microscopy. The adhesion, physical and mechanical properties of both pure components and blends have been determined, also.

Blending with effective content of VeoVa-11/MMA/2-EHA/AA copolymer (up to 20 wt.%) and thermal reactivation enhances peel strength of VA/BA copolymer, because of expeditious latex particle coalescence. The same reason makes lesser the swelling value of latex blend film for ~ 1.5 times after annealing. Low content of VeoVa-11/MMA/2-EHA/AA copolymer (up to 5 wt. %) lends VA/BA copolymer latex film best mechanical properties. Higher content of additive (>20 wt.%) increases the resistance to heat of latex blend film.

Keywords: copolymer blends, vinyl acetate copolymer, VeoVa-11 copolymer, latex films, atomic force microscopy, scanning electron microscopy.

INTRODUCTION

Water-based adhesives become increasingly important as the range of applications of polymer materials widens. Currently, worldwide efforts are aimed at reducing the volatile organic solvent content of most adhesive materials. This has promoted the search for a new generation of high-performance water-based adhesives to replace the conventional solvent-based technology [1 – 4].

Due to their potential industrial application [4 – 5] (exterior and interior architectural coatings, adhesives and paints), the polyvinyl acetate based latexes are particularly attractive. Moreover, the copolymerisation of vinyl acetate with other monomers (such as vinyl chloride [6], vinyl versatate [7], acrylate [8 – 13], vinyl propionate, methacrylate, maleate acid, fumarete acid, ethylene or acrylonitrile [1]) let to obtain useful latexes having a wide range of properties. The vinyl acetate (VA)/butyl acrylate (BA) emulsion copolymer is one of the most important industrial latexes, widely used in architectural coatings market.

VA and BA differ in their glass transition temperature [T_g(VA) = 32 °C and T_g(BA) = –54 °C]. Due to these significantly different thermal characteristics of monomers, the latexes with a wide range of properties may be synthesized. As a consequence obtained VA/BA copolymer have great interest [10].

Latex consists of polymer particles stabilised in water by surfactants. Such systems are well suited for the formation of polymer films [4]. Film formation of waterborne coatings is a complex process and may be considered as a succession of different steps, including concentration of dispersion, particle packing, particle deformation and finally their interdiffusion or autohesion [3, 12 – 18].

This film formation process has been studied by forced Rayleigh scattering [2], interferometry [3], nuclear magnetic resonance spectroscopy [4], non-radio fluorescence energy transfer [12, 13], attenuated total reflectance FT-IR, small-angle neutron scattering, freeze fracture [14], atomic force microscopes (AFM) [15 – 18] and electron microscopy (SEM and TEM) [19].

The structure of the latex film depends on the latex characteristics (nature of polymer, particle size and distribution, particle morphology, nature and amount of surfactants, etc.) and experimental conditions (annealing temperature, evaporation rate of water, etc.) [14, 15].

Preceding investigations [20] had come to the conclusion that all adhesive, mechanical and physical properties of films can be improved applying blending of VA/BA copolymer with VeoVa-10 copolymers additive. It stimulated to perform parallel investigations with VeoVa-11/MMA/EHA/AA copolymer as additive agent.

The aim of this research was to investigate the film surface structure and determine adhesion, physical and mechanical properties of VA/BA and VeoVa-11/MMA/2-EHA/AA copolymer based latex blends.

EXPERIMENTAL

All investigated materials were synthesized at the Research Experimental Laboratory of the Joint Stock Company "Achema" (Lithuania).

Water-based vinyl acetate / butyl acrylate copolymer (VA/BA = 70/30 wt.%) was used for investigations as the main film forming material. This latex was mixed with the vinyl ester of Versatic acid / metyl methacrylate / 2-ethylhexylacrylate / acrylic acid copolymer (VeoVa-11/MMA/2-EHA/AA = 60/30/7/3 wt.%).

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[*] Corresponding author. Tel.: + 370-37-451621; fax: + 370-37-353989. E-mail address: *vilma.sipailaite@ktu.lt* (V. Šipailaitė-Ramoškienė)

Compositions of the latex blends of VA/BA and VeoVa-11/MMA/2-EHA/AA copolymers, containing of VeoVa-11/MMA/2-EHA/AA from 0 to 100 wt.%, were used. A mixing temperature of 20 ±1 °C, a rotating speed of 60 rpm. and time of 5 min. were used for blends preparation.

Average particle diameters of VA/BA copolymer latex and VeoVa-11/MMA/2-EHA/AA copolymer latex (~ 240 nm and ~ 160 nm, respectively) were determined by turbidimetry techniques.

The adhesive properties were evaluated according to results of T-peel tests of adhesive joints. As substrates textile strips with area of $S = 10\ \mathrm{cm}^2$ were used. The adhesive joints were prepared according to the following two modes:

I mode. The pure polymers or their blends were applied to the textile substrate with a brush and immediately joined together under a pressure of $p = 0.25$ MPa, and pressing duration $\tau_p = 60$ s. The obtained adhesive joints were left to dry for 8 days up to full water elimination through substrate pores and adhesive film formation. After that they were tested.

II mode. Substrates after adhesive layer bonding were left to dry separately up to full water elimination. The duration of drying was 8 days. After that textile strip test pieces were reactivated by the heat in the IR ray field for 60 s and temperature $T = 100$ °C. This procedure enabled to obtain viscoelastic state of adhesive layer and to increase autoadhesion of separate layers. After that the test pieces were immediately joined under pressing conditions, as those used in the first adhesive joints preparation mode. The obtained samples were tested after being kept for 24 hours. The result of T-peel test was obtained as the average value of six samples.

The swelling value of dried latex films was evaluated according to the mass changes of samples after their immersion in the distilled water for 24 hours under ambient conditions. The samples were used with dimensions of 20×20 mm. The swelling value α during the test was calculated according to the formula:

$$\alpha = \frac{m - m_0}{m_0}; \qquad (1)$$

where m and m_0 are the mass of test sample before and after its immersing in water for 24 hours, respectively.

The surface morphology of both the pure latex and latex blends films were studied with the JEOL SM–IC25S scanning electron microscope (SEM) and NT-206 atomic force microscope (AFM) operating in a contact mode. All measurements were performed under ambient conditions. Latex films were prepared by casting onto the cleaned glass surface (1 cm^2 plates) and allowing the film to dry slowly at ambient temperature in a desiccator. Films were dried slowly over 5 days. One part of dried specimens were annealed for 1 h at 100 °C. The average thickness of dried films was ~0.1 mm. Specimens for SEM analysis were sputtered with a thin film of Ag.

The film samples were casted from the pure latex or their blends on the fluoroplastic surface. The water was completely eliminated by enough slow heat treatment at a total duration up to 14 days. The thickness of dried films was of 1 ±0.1 mm.

In order to determine the influence of heat reactivation, specimens were annealed before tensile tests for $\tau = 1$ h at the $T = 100$ °C. Six specimens were tested for each blend sample.

Mechanical measurements and T-peel tests were carried out on the tensile testing machine FP10/1 at the cross head speed of 100 mm/min.

RESULTS AND DISCUSSION

The reliance of peel strength was analysed considering adhesive joints prepared according to the *I mode* on VeoVa-11/MMA/2-EHA/AA copolymer content in blends with VA/BA copolymer.

According to the data presented in Fig. 1a, the addition of 20 wt. % of VeoVa-11/MMA/2-EHA/AA copolymer increases the peel strength of adhesive joints up to ~63 %, compared with that of pure VA/BA copolymer latex. It means that adhesive bonds between latex particles or their groups of components in blends are stronger than those between latex particles in particular agents [15]. Higher content of VeoVa-11/MMA/2-EHA/AA copolymer (>20 wt.%) in latex blends of VA/BA and VeoVa-11/ /MMA/2-EHA/AA copolymer leads to decrease of the peel strength of adhesive joints.

The reliance of peel strength of adhesive joints prepared according to the *II mode* on VeoVa-11/MMA/ /2-EHA/AA copolymer content in the blends with VA/BA copolymer was analysed, too (Fig. 1b).

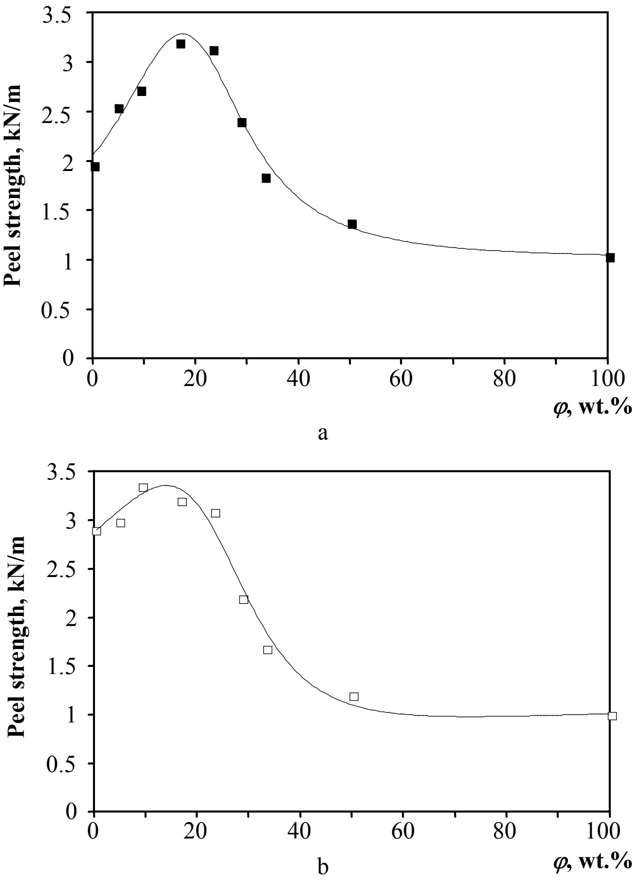
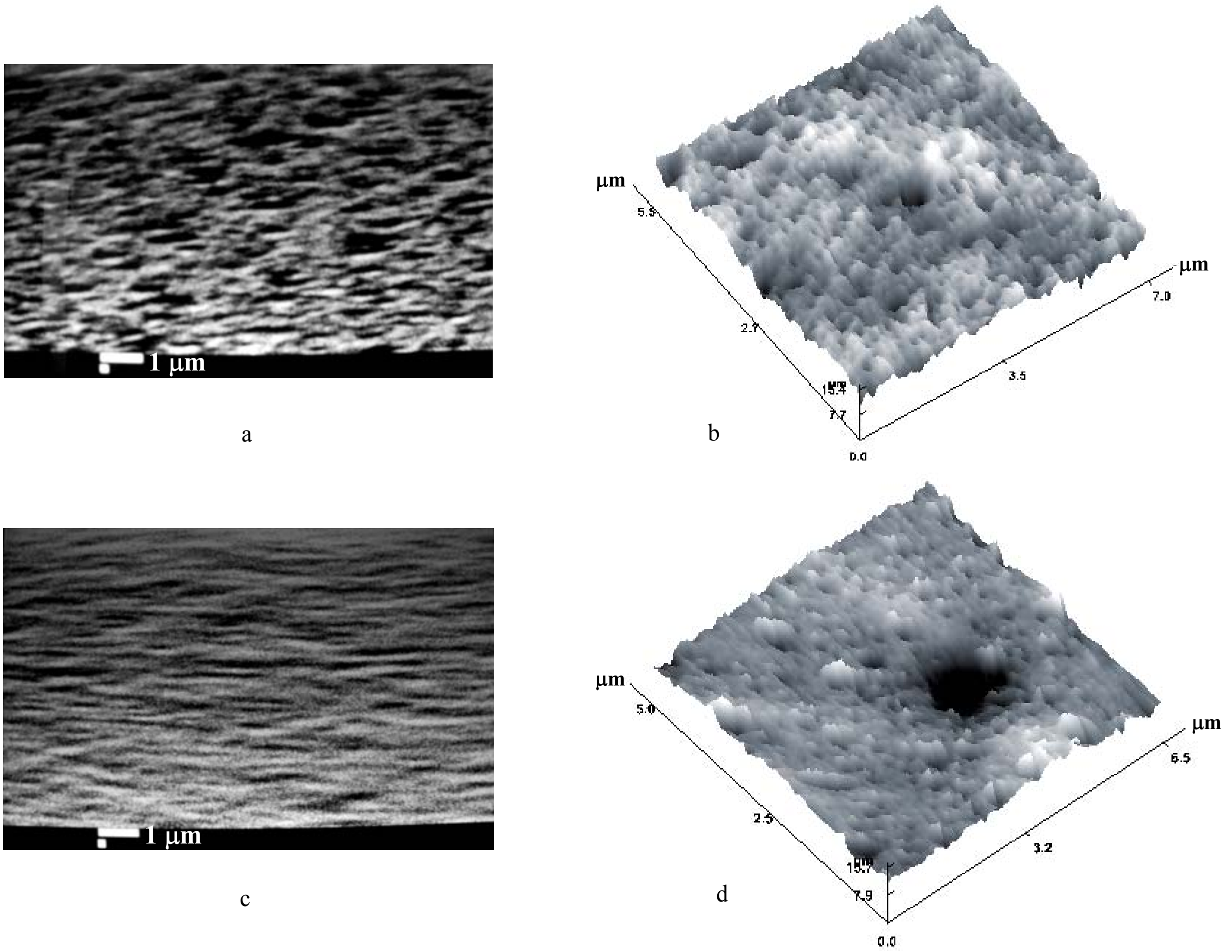


Fig. 1. The influence of VeoVa-11/MMA/2-EHA/AA content in the VA/BA latex on the peel strength of adhesive joints prepared according to *I* (a) and *II* (b) *mode*



a b

c d

Fig. 2. SEM (a, c) and AFM (b, d) images of VA/BA copolymer film surface (a, b – without annealing; c, d – annealed film)

In the blend containing approximately 10 – 20 wt.% of VeoVa-11/MMA/2-EHA/AA copolymer the peel strength of adhesive joints increases up to ~15.5 %, compared with that of pure VA/BA copolymer latex. Higher content of VeoVa-11/MMA/2-EHA/AA copolymer (>20 wt.%) in the blends with VA/BA copolymer latex results in the decrease of their peel strength.

The increase of peel strength of adhesive joints prepared according to the *II mode* is representative of low contents of VeoVa-11/MMA/2-EHA/AA copolymer (10 – 15 wt.%) in the blends with VA/BA copolymer latex. Furthermore, the peel strength of adhesive joints of pure VA/BA copolymer latex is higher near 50 % as prepared according to the *II mode*, respectively. In major the peel strength of adhesive joints prepared according to the *II mode* is caused by more expeditious latex particle coalescence than that at ambient temperature (Fig. 1).

For investigation of structure the VA/BA copolymer latex films were prepared without annealing as well as with annealing for 1 h at 100 °C. According to the results presented in Fig. 2, the structure of surface of VA/BA copolymer film prepared without annealing is composed of globules. Such structure is determined applying both atomic force microscope (AFM) and scanning electron microscope (SEM) (Fig. 2a, b). It means that the particles in the surface of film are still coalescing.

The structure of surface according to AFM and SEM investigations of the VA/BA copolymer film annealed for 1 h at 100 °C are presented in Fig. 2c and d.

Annealing accelerates the polymer macrochain diffusion between adjacent latex particles [12, 17, 18]. As result the structure of latex film surface evens out, but the pores of ~1 μm diameter appear.

Annealing during 1 h at 100 °C increases twice the swelling value of VA/BA copolymer film [20]. It can be explained by appearance of micropores in the annealed film (Fig. 2d) and, namely, these are providing channels for diffusion of water.

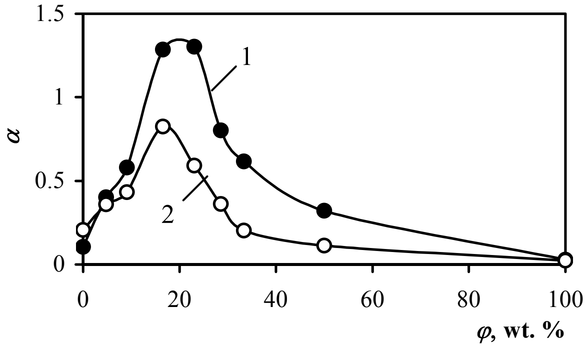
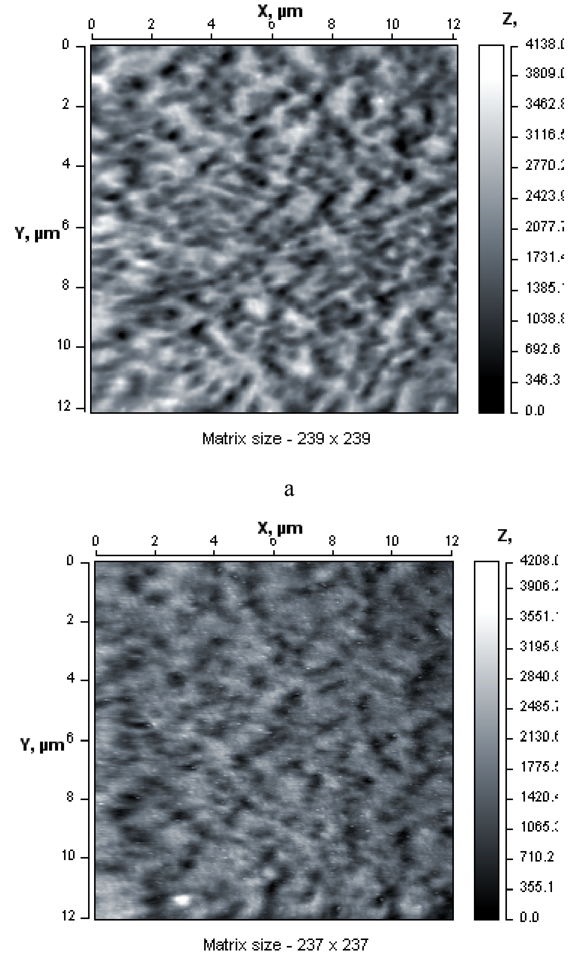


Fig. 3. Swelling value α of VA/BA copolymer film versus the modifier content φ (1 – without annealing; 2 – annealed film)

As VeoVa-11/MMA/2-EHA/AA copolymer contain 20 wt.% in the blend with VA/BA copolymer, the swelling value of latex blend film prepared without annealing increases for 12.4 times in comparison with that of pure

VA/BA copolymer film (Fig. 3). Higher content of VeoVa-11/MMA/2-EHA/AA copolymer (from 25 wt.% up to 50 wt.%) in the blend with VA/BA copolymer latex decreases the swelling value of film. But VeoVa-11/MMA/2-EHA/AA copolymer layer adsorbes on the VA/BA copolymer latex particles or their groups (Fig. 4a), and this gives a reason to endure higher swelling value of the blend than that of pure VA/BA copolymer film. Most of carboxylated groups in the layer have no intermolecular hydrogen bonds, so these groups are absorbing water molecules and increase the swelling value of film [l6].

The swelling value of annealed film of VA/BA and VeoVa-11/MMA/2-EHA/AA copolymer blend is less than that of film prepared without annealing. For example, the swelling value of annealed film with 20 wt.% VeoVa-11/MMA/2-EHA/AA content in the blend is ~1.5 times lower than that of film prepared without annealing. Nevertheless, the film of blends with different VeoVa-11/MMA/2-EHA/AA copolymer content has a higher swelling value than separated components of the blend. It can be explained by accelerated coalescence of latex particles (Fig. 4b), when amount of individual hydrophylic groups equal to absorb water molecules decreases in the surface of polymer film [16].

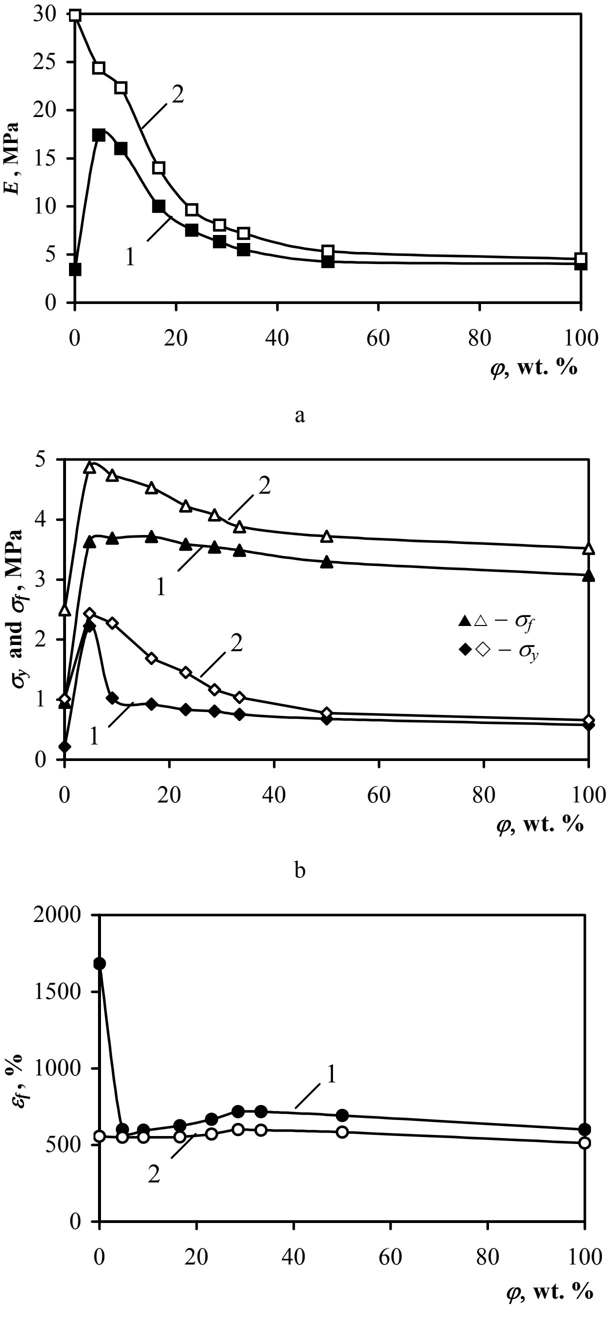


a

b

Fig. 4. AFM images of latex film of VA/BA copolymer blend with 20 wt.% content of VeoVa-11/MMA/2-EHA/AA copolymer (a – without annealing; b –annealed film)

Mechanical properties of polymer film of both VA/BA copolymer blend with VeoVa-11/MMA/2-EHA/AA copolymer and separated pure components of the blend were investigated, also (Fig. 5). It was determined that the film of pure VA/BA copolymer latex has the least Young's modulus, the least yielding and fracture stresses, and the supreme elongation at break of all investigated films prepared without annealing. The additive agents of different VeoVa-11/MMA/2-EHA/AA copolymer content in the blend with VA/BA copolymer latex alter the mentioned mechanical properties.



a

b

c

Fig. 5. Effect of annealing on mechanical properties of latex films of VA/BA copolymer blends with different content φ of VeoVa-11/MMA/2-EHA/AA copolymer (a – Young's modulus; b – yielding and fracture stresses; c – elongation at break; 1 – film prepared without annealing; 2 – annealed film)

Obtained results have shown that addition of low content of VeoVa-11/MMA/2-EHA/AA copolymer latex (up to 5 wt.%) results in the increase of Young's modulus for ~5 times. The yielding stress increases for ~10 times and the fracture stress increases for ~3.8 times, and elongation at break becomes less on ~2.8 times. Further increase of VeoVa-11/MAA/2-EHA/AA copolymer latex content (>10 wt.%) in the blend with VA/BA copolymer latex leads to diminution of Young's modulus, yielding stress and fracture stress, and to increase of elongation at break.

The highest strength characteristics of annealed films are obtained up to 5 wt.% of VeoVa-11/MMA/2-EHA/AA copolymer latex added to the blend. In the case of this content both Young's modulus and elongation at break decrease marginaly, and yielding stress increases for ~2.5 times, as well as fracture stress increases for ~2 times, compared with those properties of annealed film of pure VA/BA copolymer. Further due to increase of VeoVa-11/MMA/2-EHA/AA copolymer latex content (>10 wt.%) in the blend with VA/BA copolymer latex all the mechanical properties of annealed film begins to diminish.

Mechanical properties of annealed film of pure VeoVa-11/MMA/2-EHA/AA copolymer differ for only ~11 ÷ 14 %, in comparison with those of film prepared without annealing. It means that film of pure VeoVa-11/MMA/ /2-EHA/AA copolymer is resistant to heat, and the film of pure VA/BA copolymer does not distinguish by this property.

CONCLUSIONS

The structure of surface and the properties of latex film of VA/BA copolymer blends with VeoVa-11/ /MMA/2-EHA/AA copolymer depend on the content of additive agent and heat treatment.

Blending with effective content of VeoVa-11/MMA/2-EHA/AA copolymer (up to 20 wt.%) and thermal reactivation enhance peel strength of VA/BA copolymer, because of expeditious latex particle coalescence. The same reason makes lesser the swelling value of latex blend film for ~1.5 times after annealing. Low content of VeoVa-11/MMA/2-EHA/AA copolymer (up to 5 wt.%) lends VA/BA copolymer latex film the best mechanical properties. However, higher content of additive (>20 wt.%) increases the resistance to heat of latex blend film.

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