The Influence of the Colloidal Structure of Polymer Blends on the Adhesion Strength of Polyolefin Compositions

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The way an adhesive composition peels depends on the competing influences of its physical and mechanical properties and the reduced acidity parameter of the polymer, which forms a continuous phase. In practice, this can mean that on the outside insulation of steel pipes "dilution" of the expensive adhesive, usually a double or triple ethylene copolymer, by the less expensive polyethylene is possible, in a ratio that provides a continuous phase of "adhesion active" components. Considering the large difference in price and the fact that, in Russia, all high-quality adhesive ethylene copolymers are imported, such dilution could be an economically attractive approach.

Keywords Adhesion; blends; colloid; composition; polymers; polyolefin; strength

Introduction

Adhesive compositions on the basis of polyolefin blends were first investigated and applied at the end of the last century [1–4]. In particular, it was shown that by mixing low-density polyethylene (high pressure, LDPE) and ethylene-vinyl acetate copolymers (EVA) in the presence of a mineral filler (talc) there is an extremely large increase in the strength of adhesion of the polymer mixture to the metal (steel) compared with the raw materials [1–4]. It was later shown later [5–7] that when EVA was mixed with various concentrations of vinyl acetate units, other synergistic effects were also realised. When talc is used as filler, there is a significant increase in the strength of adhesion of a compound to the metal. The reasons for this behaviour of the compositions have been discussed in the literature [8,9], but questions about the effect of the colloidal structure of the polyolefin composition on the adhesion strength of the polymer substrate remain unresolved. It can be expected that for mixture compositions the strength of adhesive bonding will be determined by which of the copolymers – "non-adhesion active" (LDPE) or "adhesion not active" (ethylene copolymer) – forms a continuous phase in the mixture. To answer this question we chose as an object of study LDPE + EVA systems as their adhesion and physical and mechanical properties, depending on the composition of the mixture, are described in detail in the literature

[1–4,10,11]. In addition, for LDPE-EVA systems the phase diagrams have been constructed [12], which gives an idea about the compatibility of LDPE and EVA with different molecular characteristics and the content of vinyl acetate units.

Experimental

As the main objects of study we selected: low-density polyethylene (LDPE) grades 11503-070 and 15313-003, (GOST 16337-77); ethylene-vinyl acetate copolymers (EVA) grades 11104-030; EVA 11306-075, EVA 11507-375 and EVA 11808-1750, containing various amounts of ester groups (produced by JSC Sevilen, TU 6-05-1636-97); ethylene-vinyl acetate copolymers Evatane grades 20-20, 28-05; terpolymers of ethylene with maleic anhydride (EVAMA) and various vinyl acetate content grades Orevac 93-07 and 93-05; and a copolymer of ethylene with butyl acrylate (EBA) grade Lotryl 35 VA 320. The main characteristics are listed in the Table 1.

The mixtures were prepared by mixing the components in laboratory roll crushers. Samples of the compositions to be investigated were prepared by pressing them in a DV 2428 hydraulic press, in accordance with GOST 12019-66. The dimensions of the pressed plates were set by the restrictive frameworks (100 × 100 mm with a thickness of 0.9–1 mm).

The samples for adhesion testing were prepared as follows: metal plates (steel 3) were cleaned of rust and other invasive matter with sandpaper and then degreased with acetone. After this, plates were placed in the lower part of the mould in batches of six, the adhesive composition prepared earlier was spread on them and a plastic plate was laid on top of that. The double-layer composition was then pressed by the weight of the plate at 200°C for 20 min. Thereafter, without removing the load, the water cooling was switched on for 5 min. The cooling was switched off, the upper plate was raised, and the prepared samples were removed from the restrictive frameworks.

The samples of blends of LDPE 115 with EVAMA 14, EVAMA 28 and EBA were pressed for 5 min and those of blends with EVA-20 and EVA-28 for 10 min. The samples of the three-layer composition for adhesion testing were prepared as follows: metal plates were cleaned with sandpaper to remove rust and degreased with toluene, after which the liquid epoxy composition was applied with a brush. The curing process was carried out at a room temperature of 22 ± 2°C for 24 h. The rest of the method was similar to that used for two-layer systems. Compounds of the composition: ED-20:TETA (100:6) were used.

The melt flow rate of the samples was determined by a capillary viscometer, type IIRT, according to GOST 11645-73 at temperatures of 125 and 190°C. The effective viscosity was determined using molecular recognition technology (MRT – Monsanto). Experiments were carried out at a temperature of 130°C in the range of shear rates $\gamma = 3.6$ to 1226 s^{-1}. The shear rate was calculated by the formula:

$$\gamma = 0.075 \, (D_k)^{-3} \cdot U, \, (s^{-1}) \tag{1}$$

where D_k = capillary diameter and U = linear velocity of the plunger.

The viscosity was calculated by the formula

$$\eta = 22.98 \, (D_k)^{-3} \cdot P/LU \, (kPa \cdot s) \tag{2}$$

where P = pressure and L = capillary length.

The dependence of log η on log γ was estimated according to the calculated values.

Table 1. Characteristics of the polymers investigated

Characteristics	LDPE 11503-070	LDPE 15303-003	EVA 11104-030	EVA 11306-075	EVA 11507-375	EVA 11808-1750	EVA Evatane 20-20	EVA Evatane 28-05	EVAMA Orevac 93-07	EVAMA Orevac 93-05	EBA Lotryl 35 BA 320
Symbol	LDPE	LDPE	EVA	EVA	EVA	EVA	EVA	EVA	EVAMA	EVAMA	CEBA
VA content (%)	—	—	7	14	22	29	20	28	14	28	—
MA content (%)	—	—	—	—	—	—	—	—	1,5	1,5	—
BA content (%)	—	—	—	—	—	—	—	—	—	—	35
Melt flow rate (g/10 min, T = 190°C)	7.0	0.3	2.4	9.9	27.8	204	20	6.5	10.5	180	305
Melt flow rate (g/10 min, T = 125°C)				0.85	7.25	25.6	2.23	0.53	1.1	14.06	17.48
Density (kg/m³)	918	921	925	934	936	945	940	950	940	950	930
Tensile strength (MPa)	12	18	19	20	12	5	14	17	19	5	1.3
Elongation at break (%)	450	660	800	890	930	830	660	830	670	800	200
Elastic modulus (MPa)	168	186	110	61	32	12.5	31	17	62	9	3
Melting point (°C)	104	106	103	99	91	84	82	72	90	67	67
Acidity parameter of the coverage (mJ/m²)1/2	1.45	1.65	0.45	−3.05	−3.05	−1.75	−2.0	−1.15	3.8	4.1	1.8
Acidity parameter of the coverage (mJ/m²)1/2 (samples with 10% talc content)	—	—	—	—	—	—	0.15	0.5	2.75	3.75	3.0

Physico-mechanical tests were carried out on an Inspekt mini universal testing machine. The velocity of the clamps was 100 mm/min. The strength of adhesion to steel (St-3) and to the epoxy primer was evaluated by the removal of flakes of size 20×100 mm from the substrate at a angle of $180°$ and at a rate of separation of 100 mm/min on a breaking machine R-0, five times a day after the adhesive connection had been formed.

To obtain information about the colloidal structure of the mixtures of LDPE-153, LDPE-115 and various ethylene copolymers, the method of selective dissolution of the components was used. The essence of the method is multiple extraction with chloroform of the soluble part of the mixtures in a Soxhlet apparatus.

To estimate the acidity parameter, D, the surface free energy (SFE) of the components was first determined by measuring the contact angles of the samples surface by using test liquids. The test liquids used were water, dimethylformamide, glycerol, formamide, aniline, dimethylsulphoxide, saturated aqueous solutions of phenol and potassium carbonate, α–bromonaphthalene and methyleneiodide. The acidity parameter was calculated by using Berger's method [13].

The structure of the pressed samples was studied on a Solver P47 (Russia) force probe microscope. The samples were subjected to etching in chloroform and were then dried at room temperature. They were scanned in semi-contact mode. The height of scanning along the vertical axis was 200 nm; the diameter of the cantilever (tip) was 20 nm; the frequency of the cantilever oscillations was 150 kHz; the maximum scan size was 15×15 μm; and the resolution was 256×256 pixels.

Results and Discussion

As a result of the studies the concentration dependences of adhesion strength (A) of the mixtures of LDPE-153 and EVA containing 7–29% of vinyl acetate groups in relation to steel and epoxy primer were obtained. The concentration dependences of the physical and mechanical properties and selective dissolution of the materials were also obtained.

To obtain information about the structure of LDPE-153 and various types of EVA mixture, the method of selective dissolution of the mixture components in chloroform was used. It is known that LDPE and EVA with low vinyl acetate content are not soluble in chloroform under normal conditions. A higher vinyl acetate content increases the solubility of EVA in chloroform. Moreover, EVA-118 is almost completely soluble at room temperature due to the high content of polar groups and negligible crystallinity ($\approx$5%). Therefore, for the mixtures of LDPE and EVA with various vinyl acetate units, the contents were chosen such that the temperature conditions would result in complete dissolution of the copolymer (the soluble component of the mixture). Evaluation of selective dissolution of the mixtures depending on the composition is a convenient way to study the concentration ranges in which the mixture components play the role of the dispersion medium (the disperse phase), or in which both components have continuous phases (the area of phase inversion). The classic version of this curve is shown in Fig. 1.

Section A of the curve in Fig. 1 corresponds to the structure when the first component forms a continuous phase (the soluble component is a dispersion medium). Section B corresponds to the area of phase inversion. Section C corresponds to the case when the soluble component forms a continuous phase and is completely dissolved.

The concentration dependencies of the mixtures' solubility (integral and relative to the total content of the soluble component) are shown in Figs. 2 to 5. The dependences obtained allow us to determine the concentration ranges in which one of the mixture components (in this case EVA) is the dispersion medium (continuous phase). It was not possible in this
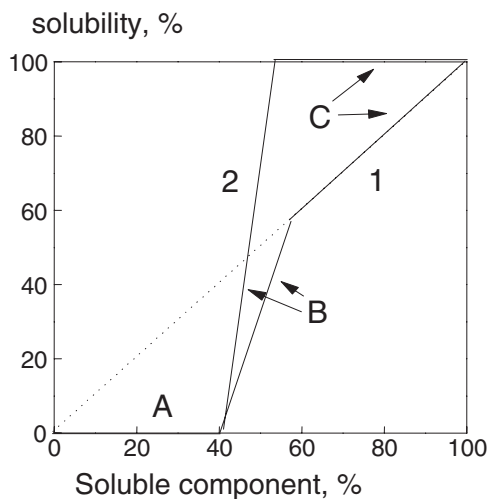
Figure 1. Theoretical dependence of the solubility of the binary mixture on the content of the soluble component. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

experiment to estimate exactly the range of the continuous phase of LDPE and the area of phase inversion, since it was necessary to choose a solvent that dissolves the polyethylene, but does not dissolve the EVA. However, at a temperature of dissolution of polyethylene such a solvent will melt also the EVA. Therefore, we can reliably estimate only the area of the continuous phase of EVA.

With a decrease in the content of vinyl acetate units in a series of the mixtures LDPE and EVA-118, LDPE and EVA-115, LDPE and EVA-113, and LDPE and- EVA-111, the area of continuous phase formed by EVA narrows. The integrated graphs as well as the concentration dependences of the solubility in relation to the total content of the soluble component illustrate this (Figs. 2–5). The solubility exceeding 100% may indicate that PE is significantly more soluble in EVA, than EVA is in LDPE [12] and, therefore, LDPE dissolved in EVA also dissolves in chloroform.
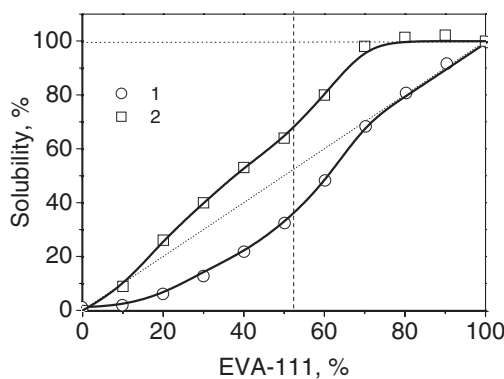

Figure 2. Concentration dependence of the solubility for a mixture of LDPE-153 and EVA-111. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.
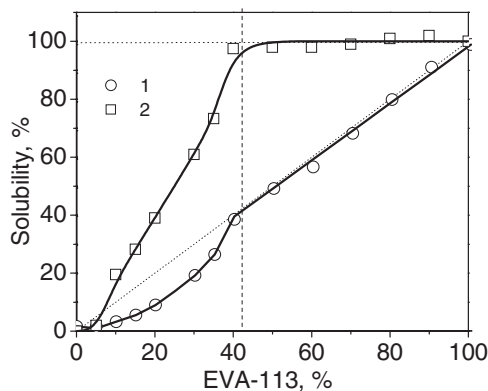
Figure 3. Concentration dependence of the solubility for a mixture of LDPE-153 and EVA-113. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

As is already known, the ratio of viscosities of polymer melts during mixing influences the formation of the colloidal structure of the mixture. The dependence of the effective viscosity on the shear rate at a measurement temperature of 130°C for the polyolefins investigated is shown in Fig. 6.

The effective viscosities for EVA-115 and EVA-118 are very dependent on the shear rate. Such curves are characteristic for polyolefins with a branched structure and a high content of the polar comonomer units [14]. The data obtained are consistent with the values of MFR measured by the standard method at 190°C (Table 1). The higher the viscosity, the lower the MFR. This result allows us to use the standard value of MFR to identify the relationship between the structural and rheological characteristics of the mixtures. One would expect that the higher the difference in MFR between LDPE and EVA, the wider the concentration range in which the less viscous component forms a continuous phase, i.e. is a dispersion medium. Such a relationship is shown in Table 2.
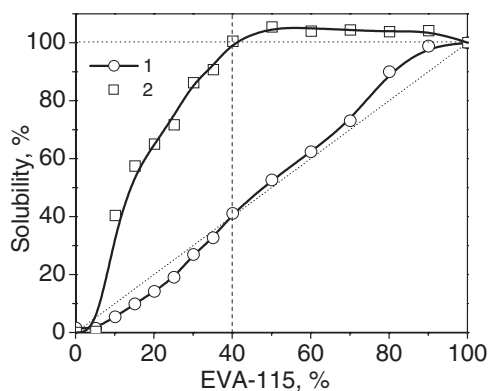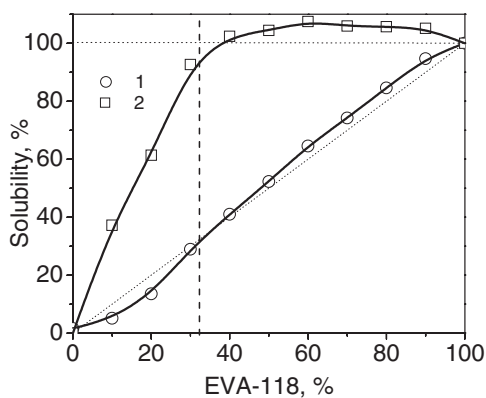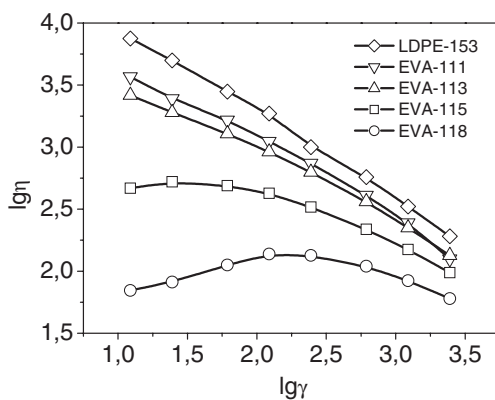

Figure 4. Concentration dependence of the solubility for a mixture of LDPE-153 and EVA-115. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

Table 2. Relationship of rheological and structural characteristics of the mixtures investigated

Mixture	|ΔMFR|	Formation of a continuous phase of the copolymer at a concentration of EVA (%)
LDPE - EVA-118	203.7	35
LDPE - EVA-115	27.5	40
LDPE - EVA-113	9.6	45
LDPE - EVA-111	2.1	70

Figure 5. Concentration dependence of the solubility for a mixture of LDPE-153 and EVA-118. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

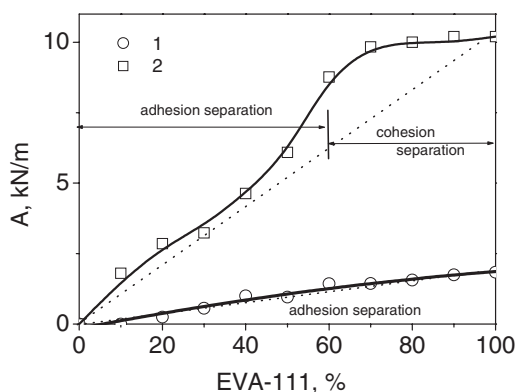**Figure 6.** Dependence of the effective viscosity on the shear rate.

Figure 7. Concentration dependence of the strength of the adhesive joint for a mixture of LDPE-153 and EVA-111. 1 – adhesive joint strength to steel; 2 – adhesive joint strength to the cured epoxy primer.

Thus, these results confirm that an increase in the difference in viscosity leads to an increase in the concentration range in which the less viscous component forms a continuous phase.

The concentration dependences of the strength of adhesion of the mixtures (A) to the steel and to the epoxy primer are presented in Figs. 7 to 10.

The dependences on the adhesion strength of the metal are S-shaped, with the exception of the LDPE–EVA-111 mixture. For this system, the change of A is close to that of the additive. This result can be explained by the fact that EVA-111 forms a continuous phase only at 70% copolymer content.

Maximum values of adhesion strength for the other systems (with a positive deviation from the additive values) can be realised in the range of EVA concentrations in which EVA, like a most "adhesive active" components, forms a continuous phase.
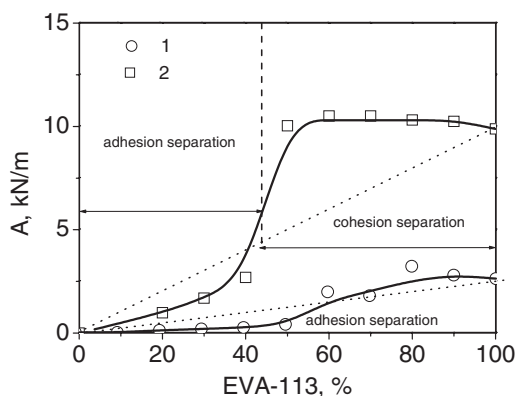

Figure 8. Concentration dependence of the strength of the adhesive joint for a mixture of LDPE-153 and EVA-113. 1 – adhesive joint strength to steel; 2 – adhesive joint strength to the cured epoxy primer.
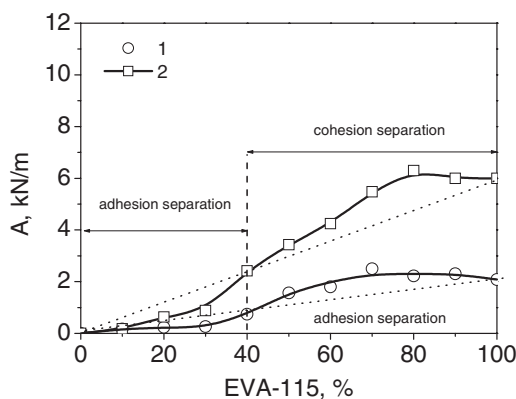
Figure 9. Concentration dependence of the strength of the adhesive joint for a mixture of LDPE-153 and EVA-115. 1 – adhesive joint strength to steel; 2 – adhesive joint strength to the cured epoxy primer.

For all systems the adhesive nature of the separation can be established visually. This is due to the low intensity of interphase interaction under the experimental conditions selected. The strength of the adhesive joint consists of both adhesion and deformation components [15]. In this case adhesion is a limiting factor and determines the nature of destruction.

The intensity of interphase interaction between polymers and metals may be interpreted within the framework of the adsorption theory of adhesion [16], on which a theory of acid-base interactions between the components of an adhesive compound develops [16]. From a practical point of view, a convenient measure of acidity (basicity) of the components of the adhesive compound is an acidity parameter (D) [13], as well as the reduced parameter of acidity ΔD, which is a function of the difference between the acidity parameters of the adhesive and the adherent [17–21]. The relation between A and ΔD for the initial materials is shown in Fig. 11.
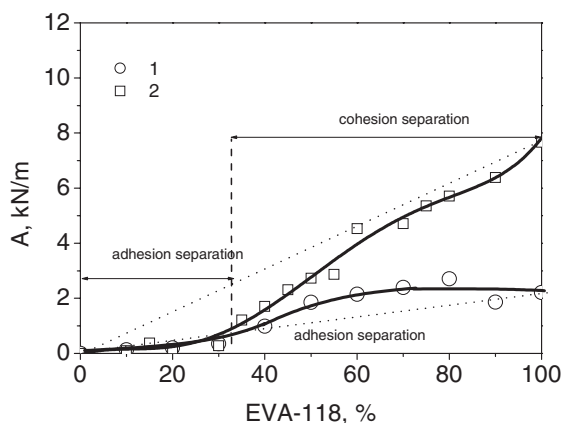

Figure 10. Concentration dependence of the strength of the adhesive joint for a mixture of LDPE-153 and EVA-118. 1 – adhesive joint strength to steel; 2 – adhesive joint strength to the cured epoxy primer.
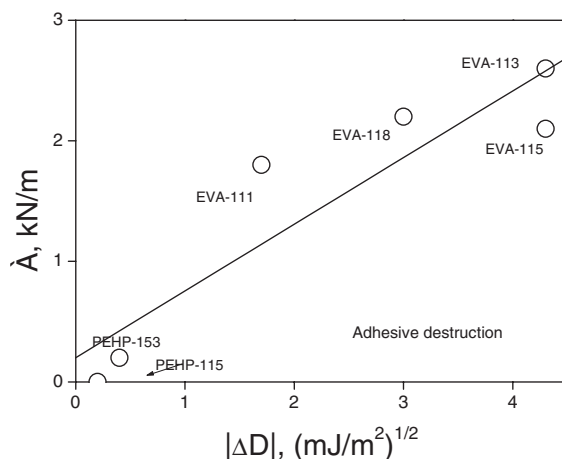
Figure 11. Relation between A and ΔD for EVA and LDPE.

As can be seen from Fig. 11, there is agreement between the values of adhesion strength and the reduced acidity parameter, with a correlation coefficient k = 0.92. Thus the adhesion strength (A) of LDPE-EVA mixtures to steel is defined by the component forming the continuous phase, while the maximum values of A are realised at the largest values of ΔD.

he results of the adhesive joint strength for assessing the systems of polyethylene– adhesive (LDPE-EVA)–epoxy primer, presented in Figs. 7–10, are generally consistent with those for the systems of polyethylene–adhesive–steel, but have some peculiarities.

Maximum values of A are also realised for mixtures with compositions in which EVA forms a dispersion medium (continuous phase). But firstly, there is a significant growth in A values with an increase in the EVA content in the mixture. Secondly, an S-shaped curve is observed only for the polymer pairs LDPE–EVA-111, LDPE–EVA-113 and LDPE–EVA-115 (Figs. 7–9). It should be noted that in the area of prevailing concentrations of LDPE in the mixtures investigated, the destruction has an adhesive nature, i.e. it realises along the interface between the adhesive and the epoxy primer. However, in the area of concentration range in which EVA has a continuous phase, the nature of separation is cohesive.

For a mixture of LDPE and EVA-118 (Fig. 10) the transition from adhesive separation to cohesion also occurs during the formation of the continuous phase by EVA-118. However, unlike the previous case, the growth of A with increasing copolymer concentration is accompanied by a negative deviation of the adhesion strength values from the additive over the whole concentration range.

The cohesive nature of destruction of the systems with epoxy adhesive can be explained by the fact that ΔD for these systems is higher (Table 1). Therefore, in these cases, the value of the adhesion strength directly at the interface is higher than the cohesive strength of the adhesive and it was this that was destroyed during the testing.

The negative deviation of the concentration dependence of A from the additive values for the system with EVA-118 is due to the fact that a mixture of LDPE and EVA-118 has minimum compatibility [12]. This affects the deformation strength properties of the compositions, i.e. the elastic modulus (E), the tensile strength (σ), the elongation at break (ε) and the specific work of destruction (w). If the mixtures of LDPE with EVA-111 (EVA-113, EVA-115) are characterised by the concentration dependences, close to that
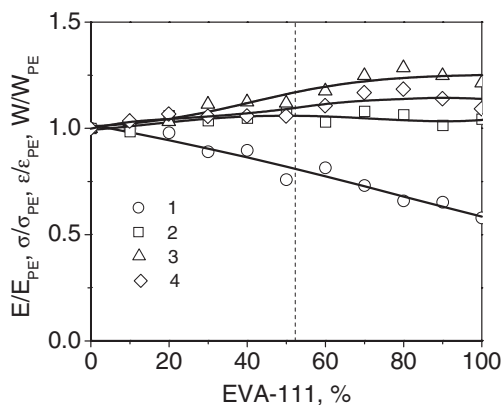
Figure 12. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-153 and EVA-111. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.

of the additive, then for a mixture of LDPE and EVA-118 a negative deviation from the additivity is observed (Figs. 12–15), until a minimum is reached (Fig. 15). This suggests low interphase adhesion and is in qualitative agreement with the variation of A (Fig. 10).

Thus, the adhesion of the mixtures investigated to steel and epoxy primer is due to the presence and concentration of polar vinyl acetate groups in EVA, which interact with functional groups of adherent by the acid-base mechanism [17–21].

A significant increase in A begins in the region of phase inversion. The maximum values of strength of adhesion to steel, as well as to the epoxy primer, are observed in the range of prevailing values of EVA when it forms a continuous phase. In the systems with a steel substrate, an adhesive component is not sufficient for the formation of a strong adhesive joint, so, visually, the destruction appears to have an adhesive nature and crosses the boundary from adhesive to steel. In the case of the epoxy substrate, a greater increase
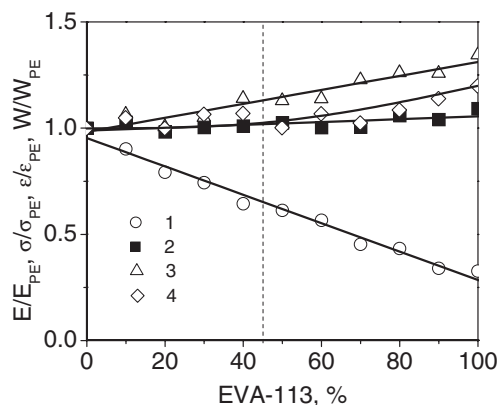

Figure 13. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-153 and EVA-113. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.
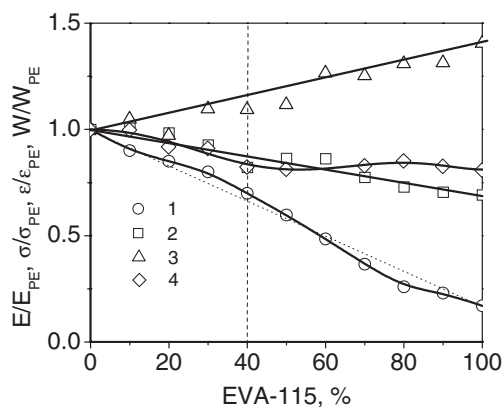
Figure 14. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-153 and EVA-115. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.

in the adhesive joint strength is observed. It is due to an increase in the difference in the acidity parameters of the contact surfaces during the transition from steel to epoxy primer. The cohesive strength of the material becomes lower than that of the adhesive component, and the destruction has a cohesive nature. For the mixtures investigated, the adhesion to the epoxy primer (fully) and to steel (in general) is consistent with the solubility graph – in the range where EVA forms a continuous phase, the adhesive strength is at a maximum. Under the chosen conditions of adhesive contact formation, the transition from adhesive destruction to cohesive destruction is determined by the nature of the substrate, which defines the intensity of interphase interaction.

For more conclusive evidence of the correctness of the above assumptions, we extended the range of polymers studied (LDPE-115, EVA-20, EVA-28, EBA, EVAMA-14, EVAMA-28). To make the results more evident, we reduced the formation time of the contact, so that the influence of the contact thermo-oxidative processes was practically excluded.
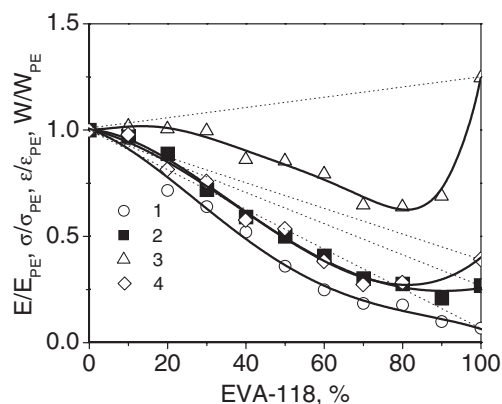

Figure 15. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-153 and EVA-118. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.
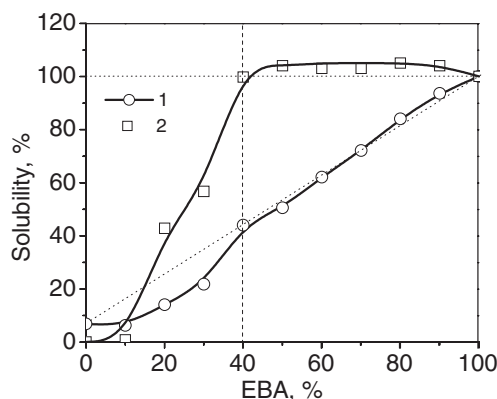
Figure 16. Concentration dependence of the solubility for a mixture of LDPE-115 and EBA. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

The concentration dependences of the solubility of the mixtures investigated (integral and relative to the total content of the soluble component) are shown in Figs. 16–20.

By analogy with the previous group of compounds, the dependence of the effective viscosity on the shear rate at a measurement temperature of 130°C for the polyolefins investigated is shown in Fig. 21.

The dependences for EVAMA-28 and EBA have the form characteristic for polyolefins, namely a branched structure, and this applies to EVA-115 and EVA-118 as well (Fig. 6).

Figure 22 shows a schematic model of ethylene, obtained from the manufacturer's website.

Table 3 shows the relationship of MFR to the structural characteristics of the mixtures at the standard measurement temperatures of 190 and 125°C. The results presented in Fig. 21 and Table 3 agree with each, other similar to those described above for LDPE-153 and EVA-111, EVA-113, EVA-115 and EVA-118.

Thus, once again the conclusion that the greater the difference in viscosity of the components, the earlier the less viscous component forms the continuous phase is confirmed.
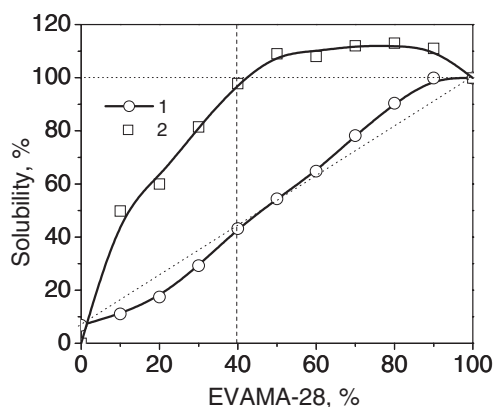

Figure 17. Concentration dependence of the solubility for a mixture of LDPE-115 and EVAMA-28. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.
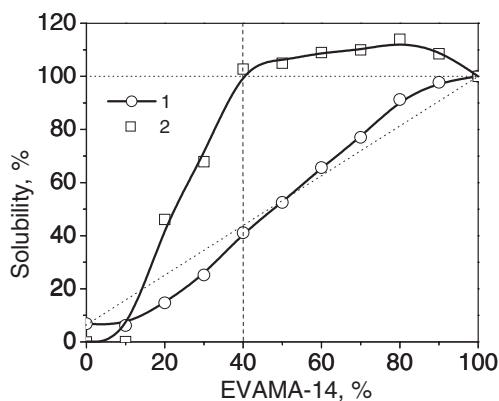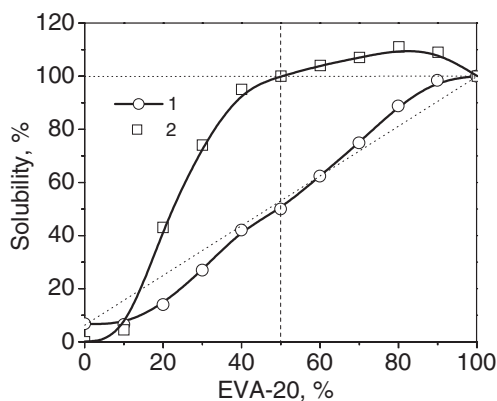
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Figure 18. Concentration dependence of the solubility for a mixture of LDPE-115 and EVAMA-14. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.
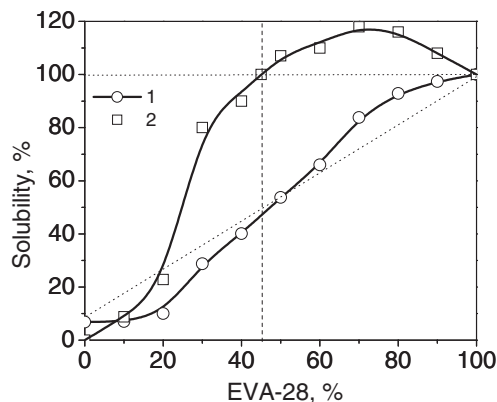

Figure 19. Concentration dependence of the solubility for a mixture of LDPE-115 and EVA-20. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

Figure 20. Concentration dependence of the solubility for a mixture of LDPE-115 and EVA-28. 1 – integral solubility; 2 – solubility in relation to the total content of the soluble component.

Table 3. Relationship of rheological and structural properties of the mixtures at a MFR measurement temperature of 190 and 125°C

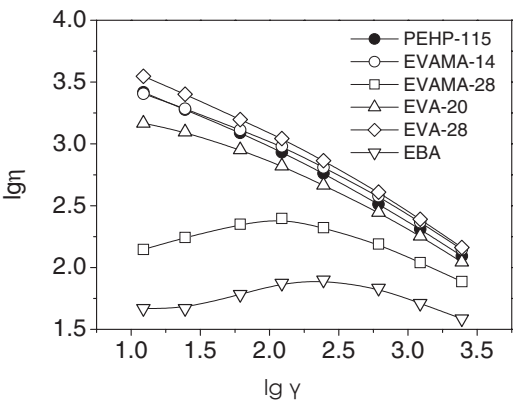| Mixture	|ΔMFR| 190°C	|ΔMFR| 125°C	Formation of a continuous phase of the copolymer at a concentration of the copolymer (%)
LDPE-115 – EBA	298	16.44	40
LDPE-115 – EVAMA-28	173	13.02	40
LDPE-115 – EVA-20	13	1.19	50
LDPE-115 – EVA-28	0.5	0.51	50
LDPE-115 – EVAMA-14	3.5	0.06	40

Figure 21. Dependence of the effective viscosity on the shear rate.
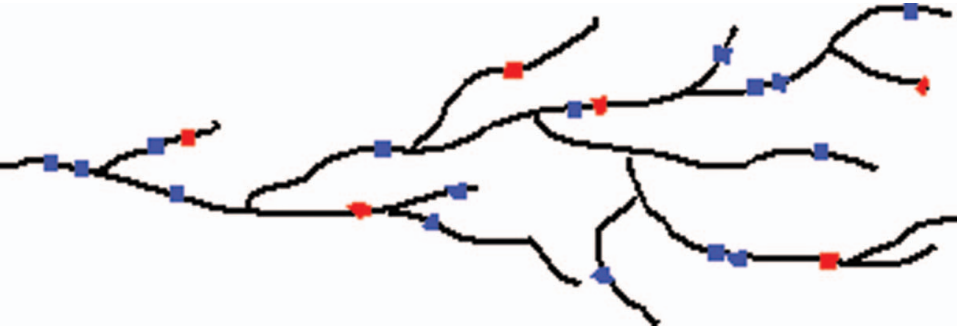

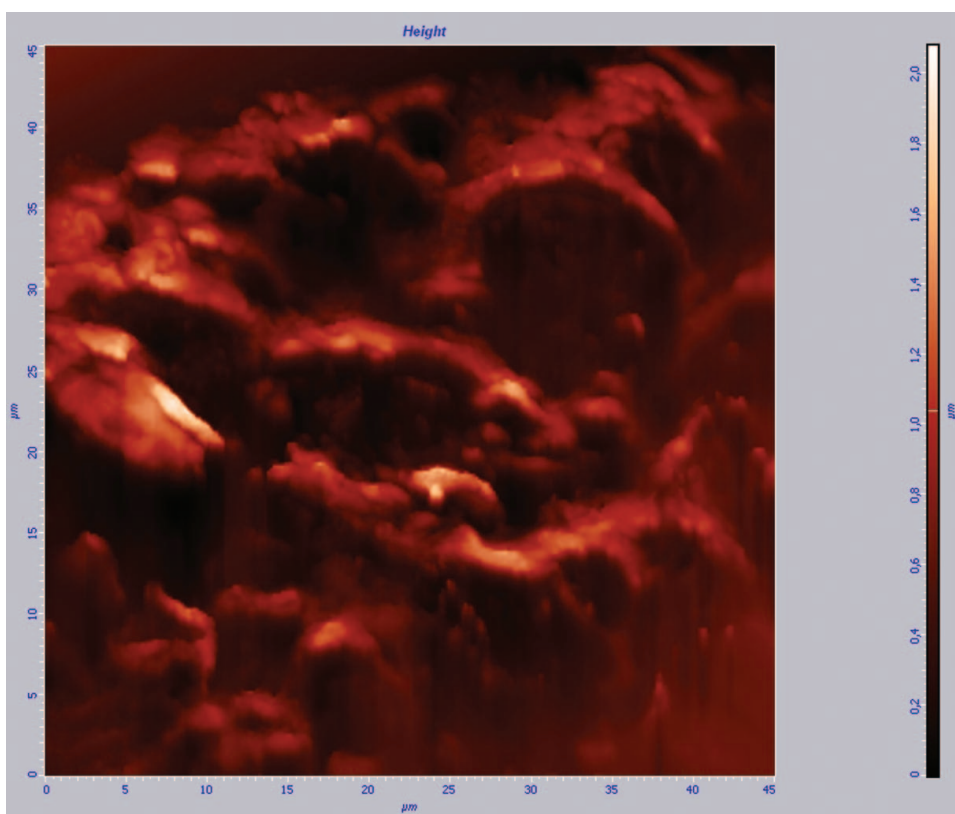**Figure 22.** Schematic model of branched copolymer of ethylene.

Figure 23. Structure of the LDPE-115–EVAMA-14 (EVAMA – 14–40%) system obtained with an atomic force microscope.

However, in this group of mixtures, EVAMA-14 looks like an exception. It can be assumed that this result is due to the fact that for this composition a matrix structure is realised (both phases are completely continuous) for the ratios of the components in the mixture considered. This makes it possible to dissolve the soluble component completely, while the dispersion medium forms at higher concentrations. This assumption is confirmed by the results obtained by the atomic force microscopy method.

Figure 23 shows a microphotograph of the LDPE-115–EVAMA-14 system containing 40% of EVAMA-14, i.e. at the point at which the strength of the adhesive bond to steel ceases to be zero (Fig. 25). There are two continuous phases: the polyethylene insoluble phase and the terpolymer soluble phase. We have assumed that the continuous phase of the copolymer begins to form a little bit later, when the value of the adhesion strength is added (Fig. 25). This follows from the microphotograph of the LDPE-115–EVAMA-14 (70%) system (Fig. 24). "Islands" of LDPE-115 dispersed phase can be seen "rising" over the soluble dispersion medium formed by EVAMA-14.

With regard to the adhesion strength of the other systems, for the compositions LDPE-115–EBA and LDPE-115–EVAMA-28, i.e. those with a less strong "adhesion active" component and the largest reduced acidity parameter, we observe that the destruction is of a cohesive nature in the range when the copolymer forms a continuous phase (Figs. 16 and 17). In the region of phase inversion and the continuous phase of LDPE-115, the adhesion
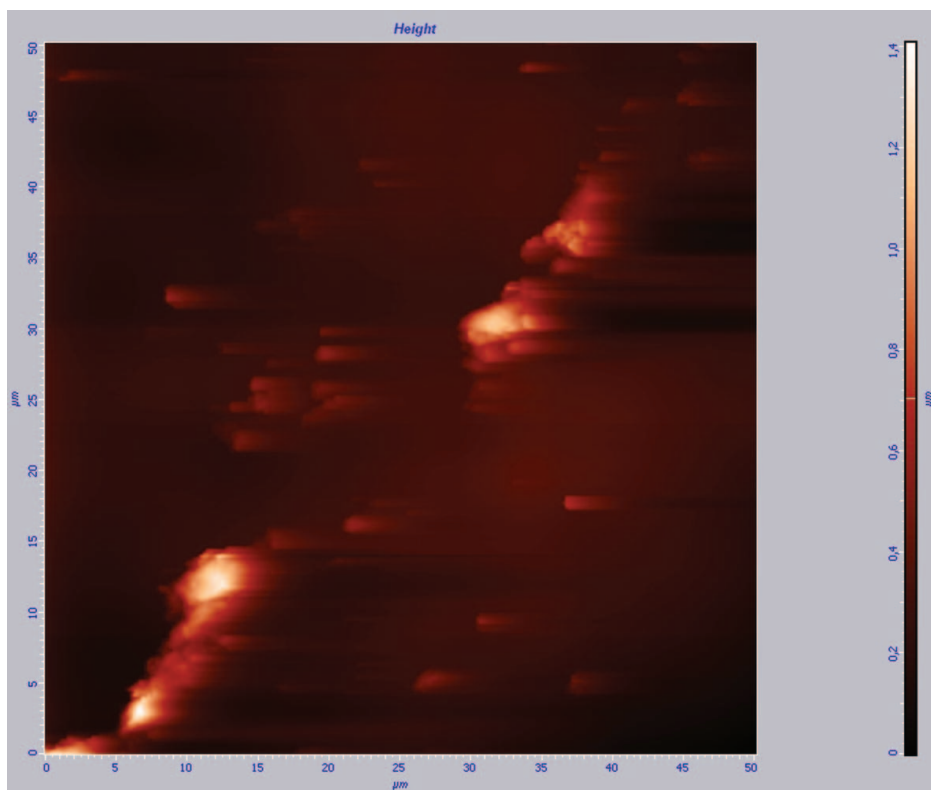
Figure 24. Structure of the LDPE-115–EVAMA-14 (EVAMA – 14–70%) system obtained with an atomic force microscope.

strength drops to zero (Figs. 26 and 27). The strength characteristics of EVAMA-28 are several times higher than those of EBA and therefore it has a higher adhesion strength. Graphs of the concentration dependences of A for both systems (Figs. 28 and 29) show that these lie below the additive values; these graphs also show the physical and mechanical
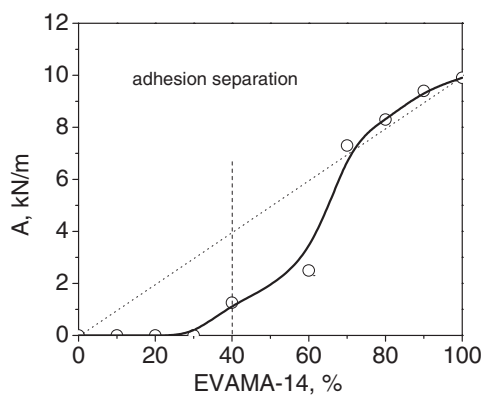

Figure 25. Concentration dependence of the strength of the adhesive joint with steel for a mixture of LDPE-115 and EVAMA-14.
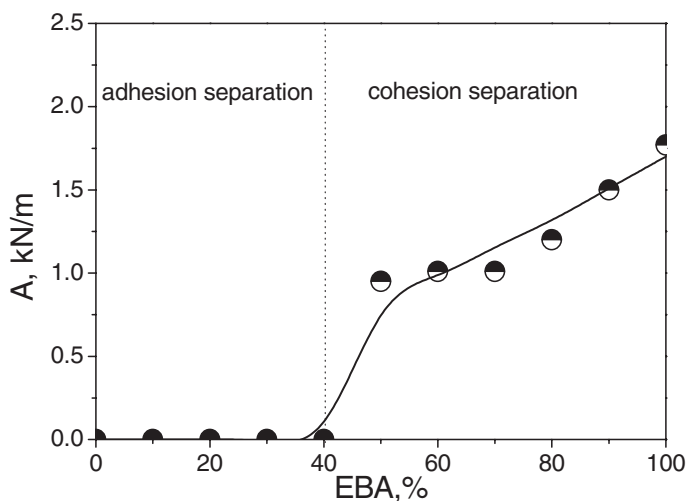
Figure 26. Concentration dependence of the strength of the adhesive joint with steel for a mixture of LDPE-115 and EBA.

properties of the systems. The values are due to the low interphase adhesion of incompatible components because of the high content of polar units in the copolymers.

Thus, for both systems, if they contain 40–100% of the copolymer, the less viscous component forms a continuous phase. As can be seen from Fig. 30, there is a correlation between the adhesion strength and the specific work of destruction for a mixture LDPE-115 and EBA in the range of cohesive destruction, with a correlation coefficient k = 0,99.

This result indicates that the concentration dependence of the adhesion strength and the nature of destruction of the LDPE-115–EBA system are determined by the physical and mechanical properties of the compositions, which, in turn, are determined by the structure of the colloidal mixture. For the LDPE-115–EVAMA-28 system, the adhesion results and the physical and mechanical properties are in qualitative agreement.
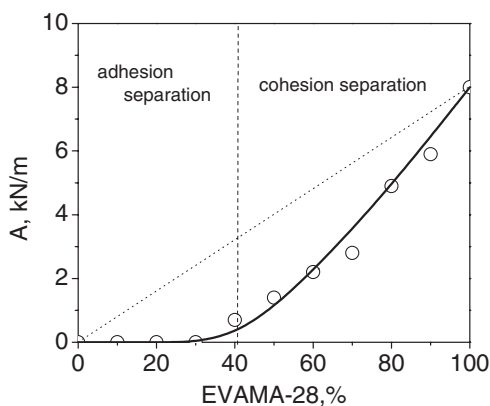

Figure 27. Concentration dependence of the strength of the adhesive joint with steel for a mixture of LDPE-115 and EVAMA-28.
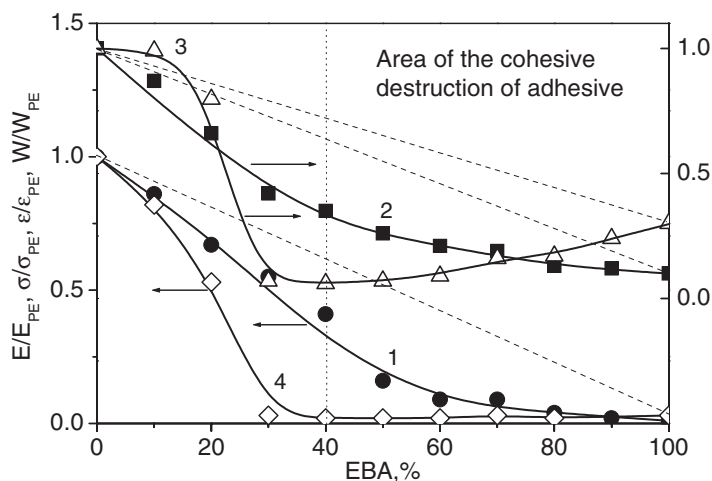
Figure 28. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-115 and EBA. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.

For the LDPE-115–EVA-20 and LDPE-115–EVA-28 systems under the selected conditions of adhesive contact formation, the separation is observed to be of an adhesive nature (Figs. 31 and 32). With decreasing polyethylene content in the composition, the adhesion strength of the connection increases, similarly to the above systems, namely LDPE-153–EVA (111–118).

The concentration dependences of the physical and mechanical properties of the LDPE-115–EVA-20 and LDPE-115–EVA-28 systems are slightly different, but in terms of adhesive destruction and low values of A, the limiting factor is the interphase interaction, characterised by the reduced acidity parameter, which has a low value (Table 1).
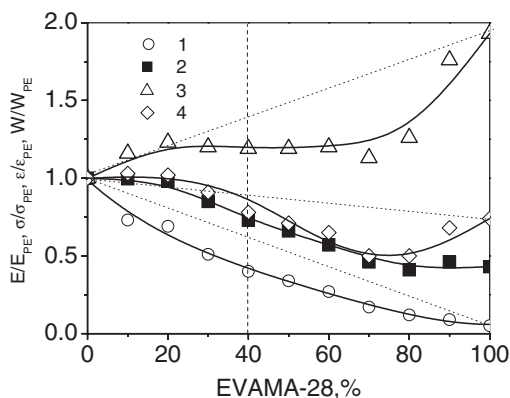

Figure 29. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-115 and EVAMA-28. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.
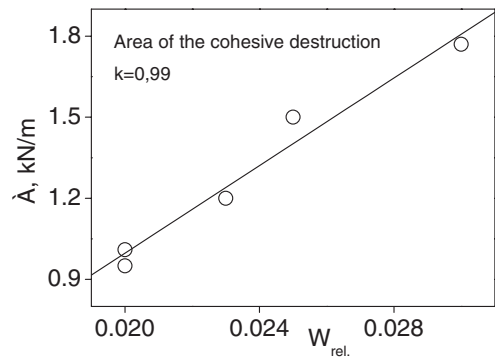
Figure 30. Correlation dependence of the strength of the adhesive joint on the specific work of destruction for a mixture of LDPE-115 and EBA.
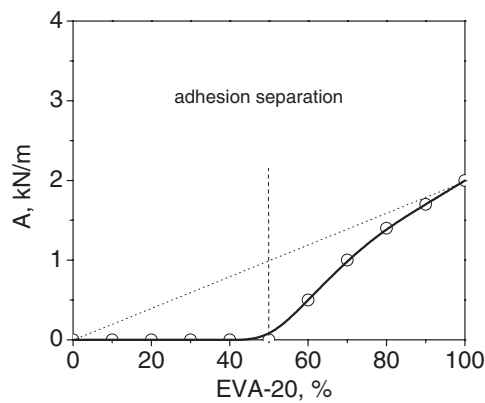

Figure 31. Concentration dependence of the strength of the adhesive joint with steel for a mixture of LDPE-115 and EVA-20.
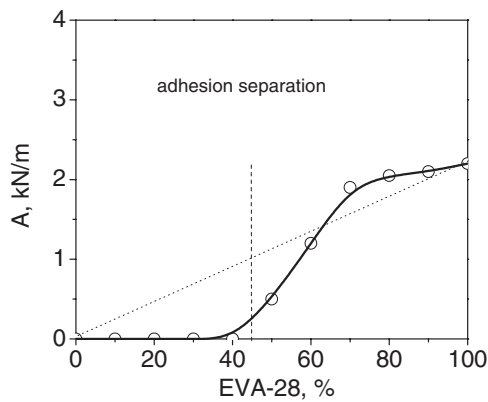

Figure 32. Concentration dependence of the strength of the adhesive joint with steel for a mixture of LDPE-115 and EVA-28.
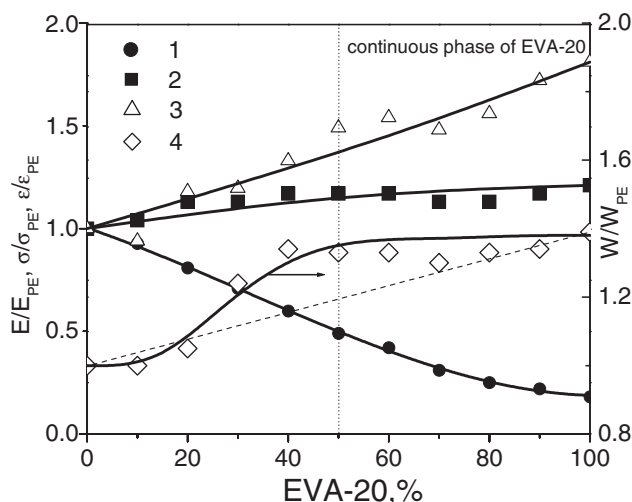
Figure 33. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-115 and EVA-20. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.

The values of adhesion strength for the systems with EVA-20, EVA-28 and EBA are approximately equal to 2 kN/m, but for EVA the separation is observed to be adhesive, and for EBA it is cohesive. At the interaction interface with steel, EBA has a higher reduced acidity parameter (Table 1), but low mechanical properties (Fig. 27). In this case, the adhesion strength exceeds the cohesion strength. As a result low values of peel stress are realised.

EVA-20 and EVA-28 have high physical and mechanical properties and a low reduced acidity parameter, so the cohesion strength exceeds the adhesion strength. In this group of mixtures the LDPE-115–EVAMA-14 system exhibits the highest strength of adhesion to steel at separation (Fig. 25). This is explained by the high value of the reduced acidity
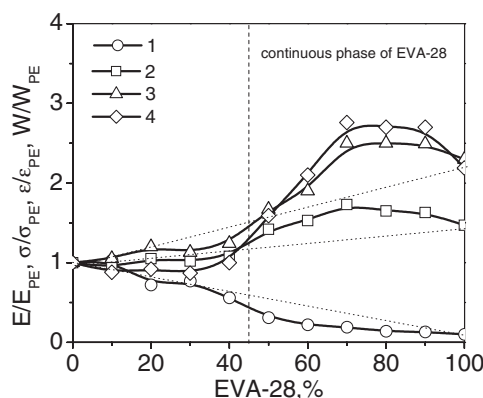

Figure 34. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-115 and EVA-28. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.
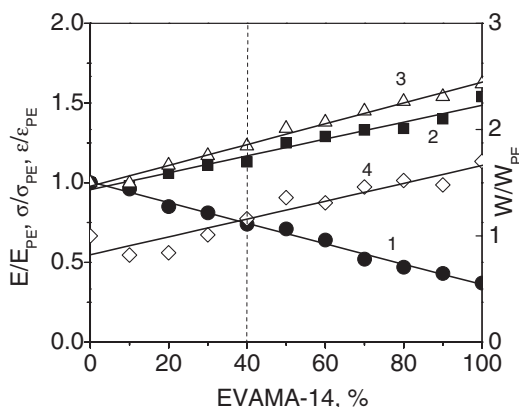
Figure 35. Concentration dependences of the physical and mechanical properties for a mixture of LDPE-1 and EVAMA-14. 1 – elastic modulus; 2 – tensile strength; 3 – elongation at break; 4 – specific work of destruction.

parameter (Table 1) and the high strength properties of the copolymer, which are presented in Figs. 33–35. In this case, it must be assumed that the adhesive nature of destruction at the values of A close to those for EVAMA-14 under conditions of cohesive separation is due to the proximity of the adhesive and cohesive components of A, and that a change in the conditions of contact formation (e.g. an increase in time) will lead to cohesive separation.

With regard to the character of the curve of concentration dependence of A for a given system, the transitional plot of the curve from zero to the high values is due to the fact that in this range a phase of LDPE as well as a phase of EVAMA-14 are continuous, and the data of atomic force microscopy method indicate that (Figs. 23 and 24). The value of A is therefore determined by the polymer, which forms a dispersion medium in the adhesive composition.

Conclusion

The way an adhesive composition peels depends on the competing influences of its physical and mechanical properties and the reduced acidity parameter of the polymer that forms a continuous phase. In practice, this can mean that on the outside insulation of steel pipes "dilution" of the expensive adhesive, usually a double or triple ethylene copolymer, by the less expensive polyethylene is possible, in a ratio that provides a continuous phase of "adhesion active" components. Considering the large difference in price and the fact that, in Russia, all high-quality adhesive ethylene copolymers are imported, such dilution could be economically attractive approach.

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