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New self-stratifying adhesives – assessment of stratification degree

Nowe samorozwarstwiające się kompozycje klejowe – ocena stopnia rozwarstwienia

New, self-stratifying adhesives composed of epoxy resin and one of selected silane terminated polymers with molecular weights in the range of 10 000–33 000 g/mol were tested. Stratification of the adhesive compositions was assessed on the basis of FTIR spectra and microscopic images of cross sections of the adhesive coatings. It has been found that it is possible to select a resin pair capable of phase separation and migration to the air/coating and coating/substrate interfaces. The best degree of stratification of resins was obtained for a composition containing an STP with the highest molecular weight and viscosity, and the lowest solubility parameter value.

Keywords: adhesives, phase separation, self-stratification

Przebadano nowe, samorozwarstwiające się kompozycje klejowe złożone z żywicy epoksydowej i jednego z wytypowanych polimerów zakończonych grupami silanowymi o masach cząsteczkowych w zakresie 10 000–33 000 g/mol. Rozwarstwienie kompozycji klejowych oceniano na podstawie widm wykonanych techniką FTIR oraz obrazów mikroskopowych przekrojów poprzecznych powłok klejowych. Stwierdzono, że istnieje możliwość dobrania par żywic zdolnych do separacji fazowej i migracji rozdzielonych faz do granicy powietrze/powłoka i powłoka/podłoże. Najlepszy stopień rozwarstwienia żywic uzyskano w wypadku kompozycji zawierającej polimer STP o największej masie cząsteczkowej i lepkości oraz o najmniejszej wartości parametru rozpuszczalności.

Słowa kluczowe: kleje, separacja fazowa, samorozwarstwienie

1. Introduction

Adhesive compositions are always developed based on their ability to bond specific materials. When selecting an adhesive for a given bond, the adhesive must adhere to the material in question, meaning that it must be able to wet the surface of the material well. In addition, the adhesive bond should have similar properties to those of the material being bonded.

In many cases, when bonding materials with different properties, a problem may arise during the selection of an adhesive that shows good adhesion to both glued surfaces. Hence, two layers of adhesive (primer and topcoat) are often used. Each of these layers contains a different binder, with an affinity for one of the materials to be connected. The disadvantage of this solution is the need to apply two layers, one after the other, which prolongs the bonding process duration. It also results in longer exposure of the people

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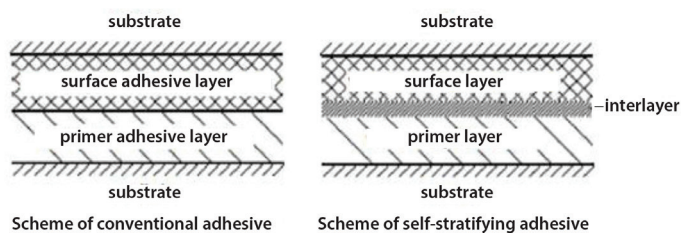


Fig. 1. Scheme of conventional and self-stratifying adhesives

Rys. 1. Schemat tradycyjnego i samorozwarstwiającego się systemu klejowego

conducting the bonding work to solvents or other harmful substances.

A new concept that can be adopted is the phenomenon of self-stratifying compositions [1–6]. Its principle rests on obtaining two layers that perform separate functions during one operation of coating or adhesive product application. The composition must be based on a mixture of resins with limited compatibility, which, when applied to the substrate, undergo phase separation and stratification to form two layers, each enriched in one of the resins (Fig. 1). This makes it possible to provide properties that were previously obtained only when two separate products were applied layer by layer. An additional advantage is the improvement of interlayer adhesion due to the presence of an interlayer containing a mixture of the resins used in the product [7]. The use of immiscible binders in adhesive technology creates the possibility of producing adhesive products with a new range of properties [8, 9]. Heterogeneity of the structure of such polymeric materials improves their technical properties and provides them with specific characteristics.

Another important direction in the adhesives and sealants industry is the use of raw materials that comply with environmental regulations and yet are not inferior in properties to previously used raw materials [10]. The presence of organic solvents, isocyanates or tin-containing catalysts is being reduced in adhesive compositions. So-called STPs (silane terminated polymers), or polyethers terminated with silane groups, are becoming increasingly popular. These are organic polymers built from a polyether chain linked to protective silane groups through an ether or urethane bond. Thus, they combine the advantages of both silicones and polyethers. The proposed STPs show very good flexibility and UV resistance, as well as good mechanical properties.

The aim of the present study was to select resin pairs with limited compatibility, which undergo phase separation and stratification after application to the substrate. Epoxy resin/polymer STP compositions were studied. One epoxy resin with hardener and 4 STPs of different molecular weights were used.

2. Experimental

2.1. Characterization of raw materials and sample preparation

Four STPs differing mainly in molecular weight and viscosity and one epoxy resin were selected for the study. The characteristics of the STPs studied, including molecular weight, viscosity and solubility parameters [11] are shown in Table 1. A summary of the FTIR

Table 1. Characteristics of STPs studied

Tabela 1. Charakterystyka badanych polimerów STP

Symbol	Molecular weight [g/mol]	Viscosity [mPas]	Solubility parameter [MPa ^{1/2}]
H1	18 000	9 000–15 000	21.4
H2	10 000	7 000–8 000	21.4
H3	33 000	30 000–50 000	19.6
H4	15 000	8 000–12 000	20.9

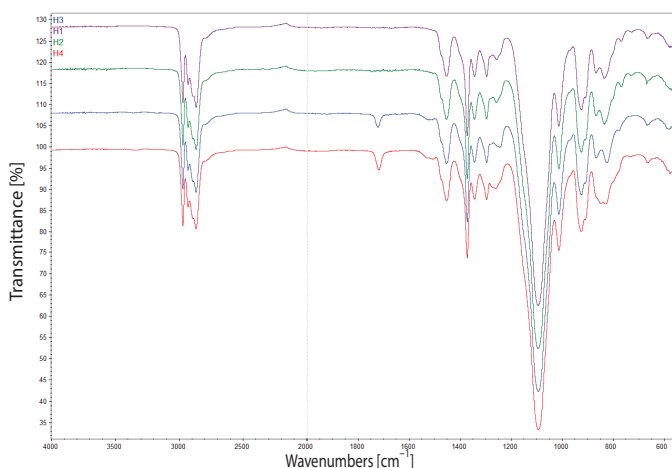


Fig. 2. FTIR spectrum of STPs studied

Rys. 2. Widmo FTIR badanych polimerów STP

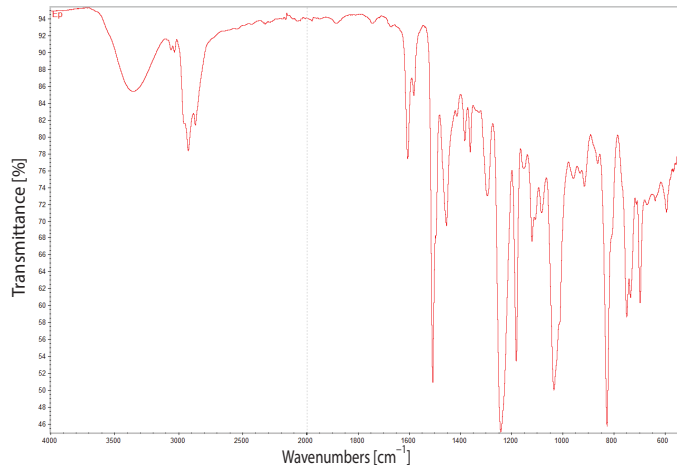


Fig. 3. FTIR spectrum of cured epoxy resin

Rys. 3. Widmo FTIR utwardzonej żywicy epoksydowej

spectra of the selected STPs is shown in Fig. 2. The epoxy resin is a reaction product of bisphenol A and epichlorohydrin in solution form in organic solvents with an epoxide number in the range of 0.49–0.51 mol/100 g. The viscosity of epoxy resin is in the range of 200–400 mPas. The solubility parameter of the epoxy resin was 20.7 MPa^{1/2} [12]. An isophoronediamine solution was used as the curing agent of the epoxy resin. The FTIR spectrum of the cured epoxy resin is shown in Fig. 3.

Preparation of the adhesive compositions for testing consisted of mixing the epoxy resin with the selected STPs in the

appropriate ratio. Each composition also contained a hardener in a stoichiometric amount relative to the epoxy resin. The compositions prepared contained epoxy resin and an STP in ratios of 50 : 50 and 70 : 30.

The coatings for the tests were prepared by applying the prepared composition to polyester and aluminium substrates using an applicator with a gap width of 240 μm or 2000 μm . The degree of stratification of the resins was determined after 7 days of conditioning at room temperature.

2.2. Methodology

The degree of stratification of the resins and polymers was determined by infrared spectroscopy with the ATR-FTIR technique using a Thermo Scientific Nicolet iS10 spectrophotometer. The spectra of the top and bottom surface of the free coatings obtained from the prepared adhesive compositions were determined. Before analysing the spectra of the self-stratifying compositions, spectra of the individual STPs and the epoxy resin were taken to determine the areas in which the characteristic bands of the resin group occur. Based on the intensity of the bands characteristic of the individual components of the composition – 1370 cm^{-1} ($\delta_{\text{aliphatic}}$) for STPs and 1509 cm^{-1} ($\nu_{\text{aromatic ring}}$) for the epoxy resin – the content of the resins in the top and bottom layers was calculated.

The cross-sectional structure of the adhesive composition coatings was analysed using a Hitachi SU8010 type scanning electron microscope (SEM; Hitachi, Japan, 2011). Basic conditions for microscope observations: detector type – SE (second electron), accelerating voltage – 20 kV, current intensity – ca. 10 microamperes, so-called working distance – 8–9 mm.

2.3. Discussion

The widespread use of STPs in the adhesives and sealants industry is driving further research that aims to provide better characterisation of these polymers and thus match them to specific applications. Their thermodynamic parameters have been determined, including the solubility parameter by inverse gas chromatography (IGC) [11]. These parameters depend on elements of the structure and properties of macromolecular compounds, and can at the same time be used to interpret or predict phenomena such as miscibility, solubility or adsorption [5, 13]. Ongoing research also allows expanding the possibilities of their use in increasingly new adhesive compositions.

The study used an isophoronediamine-cured epoxy resin and four STPs differing in structure, molecular weight, and viscosity. Each composition contained an STP in addition to the epoxy resin with hardener. The epoxy resin should accumulate in the bottom layer and form a priming layer for the substrate, while the STP should collect on the surface, guaranteeing adequate adhesive properties.

Table 2 summarises the results of resin stratification determinations for adhesive compositions in which the mass ratio of resins is 50 : 50 or 70 : 30, which were applied to a polyester film substrate. In the case of the H1 polymer, regardless of the mutual ratio of resins, stratification was imperceptible. The surfaces of the top and bottom layers consisted of a mixture of both resins. For the other three STPs, an increase in the content of STP on the surface of the top layer could be observed, while that of epoxy resin increased on the surface of the bottom layer, especially at a 70 : 30 ratio of epoxy resin to STP. For these systems, the content of STPs on the surface of the top layer was 60.3%, 70.3% and 72.2% for polymers H2, H3 and H4, respectively.

Table 2. Degree of stratification of resins in adhesives – polyester substrate, coating applied with a 240 μm applicator

Tabela 2. Stopień rozwarstwienia żywic w kompozycjach klejowych – podłoże poliestrowe, powłoka nanoszona aplikatorem o szerokości szczeliny 240 μm

System	Resin mass ratio	Surface tested	Epoxy resin content ^a [%]	Content of STP ^a [%]
EP : H1	50 : 50	top	48.3	51.7
		bottom	51.7	48.3
	70 : 30	top	49.4	50.6
		bottom	50.6	49.4
EP : H2	50 : 50	top	52.7	47.3
		bottom	46.2	53.8
	70 : 30	top	39.7	60.3
		bottom	58.7	41.3
EP : H3	50 : 50	top	38.7	61.3
		bottom	63.2	36.8
	70 : 30	top	29.7	70.3
		bottom	72.6	27.4
EP : H4	50 : 50	top	53.2	46.8
		bottom	46.3	53.7
	70 : 30	top	27.8	72.2
		bottom	100.0	0.0

^a On the surface of the layer.

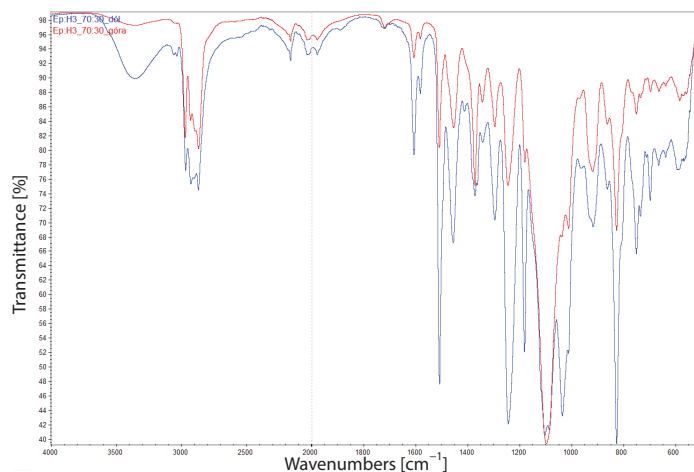


Fig. 4. FTIR spectra of the top and bottom surface layer of adhesive EP : H3 (ratio of resins 70 : 30) – polyester substrate

Rys. 4. Zestawienie widm FTIR powierzchni górnej i dolnej warstwy powłoki klejowej EP : H3 (stosunek żywic 70 : 30) – podłoże poliestrowe

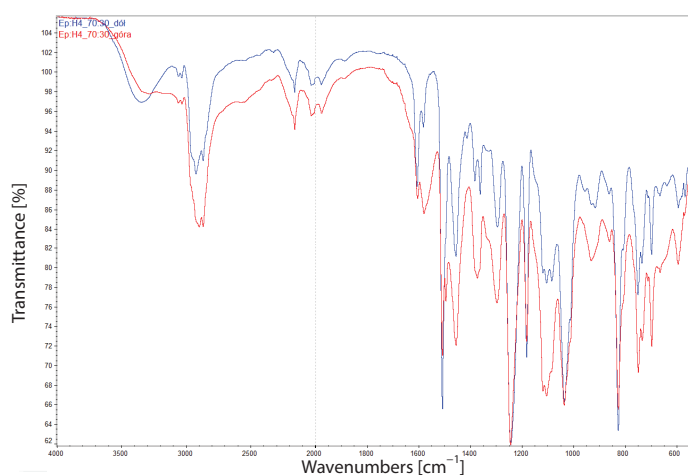


Fig. 5. FTIR spectra of the top and bottom surface layer of adhesive EP : H4 (ratio of resins 70 : 30) – polyester substrate

Rys. 5. Zestawienie widm FTIR powierzchni górnej i dolnej warstwy powłoki klejowej EP : H4 (stosunek żywic 70 : 30) – podłoże poliestrowe

The EP : H3 and EP : H4 systems showed the highest epoxy resin content on the surface of the bottom layer (Fig. 4, 5).

Table 3 shows the results of resin stratification rates for all tested compositions after application to an aluminium substrate using 240 μm and 2000 μm gap width applicators. In most adhesive compositions, with the exception of EP : H1, increasing the thickness of the adhesive coating led to a higher degree of resin stratification. As in the case of the polyester substrate, increasing the epoxy resin content in the composition had a positive effect on the degree of stratification. The highest degree of stratification was observed for the EP : H3 system (Fig. 6). At a 50 : 50 resin mass ratio, the epoxy resin content on the bottom layer surface, depending on the coat-

ing thickness, is 78.2% and 81.6%. In contrast, the surface of the top layer predominantly contains STP, with contents of 63.8% and 68.4%. The EP : H4 system on the aluminium substrate, regardless of the coating thickness, does not undergo any stratification, and behaves differently than when applied to the polyester substrate (Fig. 7).

The most favourable adhesive compositions among those tested are those that, when applied to a substrate, spontaneously undergo phase separation and stratification in such a way that the surface of the bottom layer contains predominantly an epoxy resin acting as a priming layer for the substrate, while the surface of the top layer contains a polymer that imparts adhesive properties to the coating. The formation of layered structures can also be observed in micro-

Table 3. Degree of stratification of resins in adhesives – aluminium substrate

Tabela 3. Stopień rozwarstwienia żywic w kompozycjach klejowych – podłoże aluminiowe

System	Resin mass ratio	Thickness of a liquid layer [μm]					
		240			2000		
		surface tested	epoxy resin content ^a [%]	content of STP ^a [%]	surface tested	epoxy resin content ^a [%]	content of STP ^a [%]
EP : H1	50 : 50	top	38.1	61.9	top	47.5	52.5
		bottom	59.2	40.8	bottom	52.7	47.3
	70 : 30	top	31.8	68.2	top	41.3	58.7
		bottom	62.4	37.6	bottom	61.2	38.8
EP : H2	50 : 50	top	43.5	56.5	top	35.0	65.0
		bottom	58.1	41.9	bottom	59.8	40.2
	70 : 30	top	48.0	52.0	top	34.8	65.2
		bottom	51.9	48.1	bottom	61.2	38.8
EP : H3	50 : 50	top	36.2	63.8	top	31.6	68.4
		bottom	78.2	21.8	bottom	81.6	18.4
	70 : 30	top	33.2	66.8	top	29.0	71.0
		bottom	93.3	6.7	bottom	95.4	4.6
EP : H4	50 : 50	top	53.9	46.1	top	53.2	46.8
		bottom	45.4	54.6	bottom	46.5	53.5
	70 : 30	top	49.3	50.7	top	52.4	47.6
		bottom	50.7	49.3	bottom	46.4	53.6

^a On the surface of the layer.

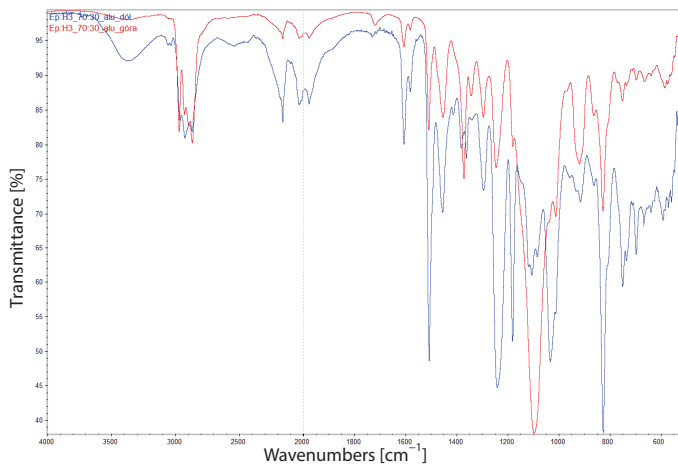


Fig. 6. FTIR spectra of the top and bottom surface layer of adhesive EP : H3 (ratio of resins 70 : 30) – aluminium substrate

Rys. 6. Zestawienie widm FTIR powierzchni górnej i dolnej warstwy powłoki klejowej EP : H3 (stosunek żywic 70 : 30) – podłoże aluminiowe

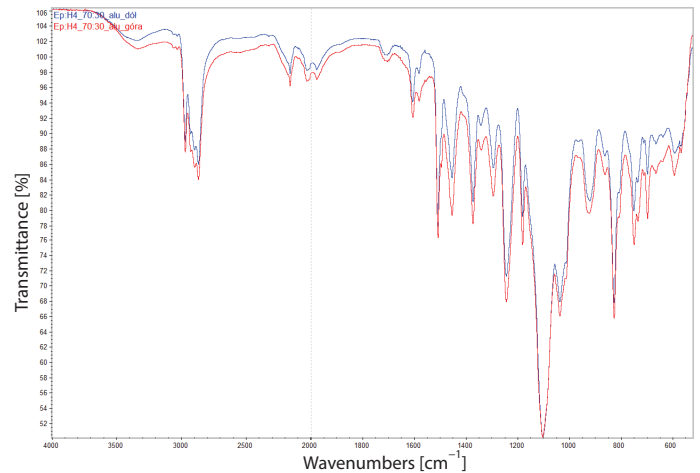


Fig. 7. FTIR spectra of the top and bottom surface layer of adhesive EP : H4 (ratio of resins 70 : 30) – aluminium substrate

Rys. 7. Zestawienie widm FTIR powierzchni górnej i dolnej warstwy powłoki klejowej EP : H4 (stosunek żywic 70 : 30) – podłoże aluminiowe

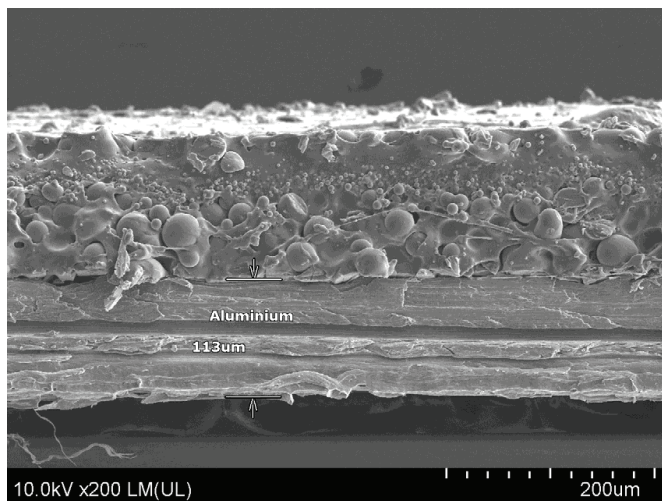


Fig. 8. Cross-section of adhesive EP : H3 70 : 30 on aluminium substrate

Rys. 8. Przekrój poprzeczny powłoki klejowej EP : H3 70 : 30 na podłożu aluminiowym

scopic photos of the adhesive coatings' cross sections. In Fig. 8, which shows a photo of a cross-section of a coating composed of EP : H3, differences between the structure of the top and bottom layers can be seen. The boundary between the layers is not very clearly marked but this is one of the advantages of self-stratifying compositions. Very good interlayer adhesion is thus ensured. This adhesion is better compared to the adhesion of layers applied separately, one after the other.

For comparison, Fig. 9 shows a microscopic photo of a coating from a composition that was characterised by a lack of stratification. The coating is homogenous across its entire cross-section, and no differences in the structure of individual layers are observed. Conclusions from observing and evaluating stratification based on microscopic images of coating cross-sections confirm the results obtained by FTIR analysis.

Based on the results obtained, it was found that the best degree of resin stratification was obtained for the composition containing the STP with the highest molecular weight and viscosity and the lowest

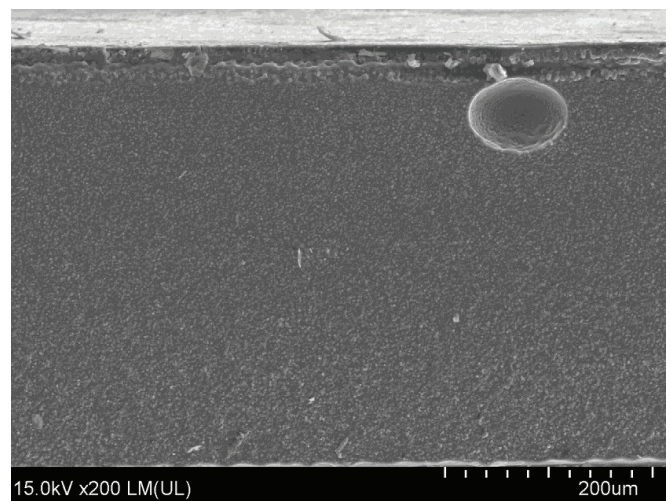


Fig. 9. Cross-section of adhesive EP : H4 70 : 30 on aluminium substrate

Rys. 9. Przekrój poprzeczny powłoki klejowej EP : H4 70 : 30 na podłożu aluminiowym

solubility parameter value. Such a result was obtained regardless of the type of substrate to which the adhesive composition was applied.

3. Conclusion

A new concept for obtaining multifunctional self-stratifying adhesives makes it possible to obtain two layers performing separate functions during a single application of the adhesive product. The composition of such a product must be based on a mixture of resins with limited compatibility, which after application to the substrate undergo phase separation and stratification to form two layers, each of which is enriched in one of the resins. The most favourable adhesive compositions among those tested are those which, after application to the substrate, undergo phase separation and stratification on their own in such a way that the surface of the bottom layer contains predominantly an epoxy resin acting as a priming layer for the substrate, while the surface of the top

layer contains a polymer that imparts adhesive properties to the coating.

Compositions consisting of epoxy resin and one of four STPs, differing in molecular weight, viscosity and solubility parameter, were tested. The best degree of resin stratification was obtained for the composition containing an STP with the highest molecular weight and viscosity and the lowest solubility parameter value.

The study represents a preliminary evaluation of the stratification of adhesive compositions. In order to assess the possibility of their practical application, it is necessary to carry out additional tests of an applicative nature, taking into account a number of important parameters. These include: the stability of the resin mixture prior to application, the kinetics of stratification and the time taken to achieve the maximum degree of stratification, the relationship between stratification and ambient temperature, the bonding strength of the bonded system after reaching full stratification in comparison with a two-coat system for different pairs of materials.

Self-stratifying adhesives will have the potential to be used for bonding multiple surfaces, i.e. concrete, screeds of various types on the one hand, and wood, strips, boards, MDF, linoleum, various types of carpeting on the other hand.

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CRedit authorship contribution statement

Ewa Langer: Conceptualization, Funding acquisition, Investigation, Supervision, Writing – original draft, Writing – review & editing.

Katarzyna Suchoń: Conceptualization, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing.

Grażyna Kamińska-Bach: Investigation, Methodology, Writing – original draft, Writing – review & editing.

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