https://doi.org/10.32010/mpmc2024.001

PREPARATION OF ADHESIVE COMPOSITION BASED ON ALLYL PROPIONATE-STYRENE-MALIC ANHYDRIDE TERTIARY COPOLYMER

Fariz Amirli[1], Rasmiyya Mammadova[2], Aman Eyvazov[3]

[1,2,3]Azerbaijan State Oil and Industry University, Baku, Azerbaijan
[1] fariz.emirov@asoiu.edu.az, http://orcid.org/0000-0002-9095-2982
[2] rasmiyyamammadova76@gmail.com, http://orcid.org/0009-0007-8698-8302
[3] aman.eyvazov@mail.ru, http://orcid.org/0009-0007-0318-1029

ABSTRACT

Adhesive compositions based on allyl propionate-styrene-maleic anhydride ternary copolymer and ED-20 epoxy resin were prepared and some physical and physico-chemical properties of these adhesive compositions were determined.

Adhesive compositions were prepared in different ratios of allyl propionate-styrene-maleic anhydride ternary copolymer and ED-20 epoxy resin (10,15, 20, 25, 30 m.f. copolymer for 100 m.f. ED-20 epoxy resin).

The property of bonding duralumin plates of the glue obtained by curing under different conditions was studied. It was determined that the sliding fracture resistance of the adhesive compositions prepared in different mass ratios of the copolymer and ED-20 epoxy resin for duralumin plates was higher in the ED-20:CP=100:25 ratio. When the adhesive composition obtained in this mass ratio is cured at 140, 160, and 180 ^{o}C for 2 hours, the sliding fracture resistance for duraluminum plates was 13.8, 13.9, and 14.4 MPa.

The tensile fracture resistance and dielectric properties of the adhesive composition prepared in the ratio of ED-20:CP=100:25 were determined. The tensile fracture resistance of the adhesive composition prepared in this ratio was 2.13 MPa, the dielectric permeability was 1.8 (at a frequency of 10^6 Hs) and the angular tangent of the dielectric loss was $45 \cdot 10\text{-}3$ (at a frequency of 10^6 Hs). The degree of swelling of the adhesive compositions prepared by curing in different mass ratios in different solvents was determined. The degrees of swelling of the adhesive composition prepared by curing in a mass ratio of 100:25 in toluene, chlorobenzene, 1,4-dioxane, and butylacetate are 0.63, 0.67, 0.75, and 4.19% respectively.

Keywords: allyl propionate, styrene, maleic anhydride, ternary copolymer, epoxy resin, adhesive composition, swelling degree, dielectric permeability.

Introduction

Since the areas of application of adhesive compositions are wide, the preparation of adhesive compositions with new ingredients for bonding various surfaces is always at the center of attention as an actual problem. While glues made based on natural rubber, albumin, and casein have low weather resistance, these indicators of synthetic adhesive compositions are very high.

During the preparation of adhesive compositions, it is necessary to fulfill the following requirements: no release of volatile substances during curing, no toxicity, wear resistance, flexibility, resistance to water and atmospheric effects, and sufficient lifetime. Adhesive compositions are thermoreactive and thermoplastic depending on the nature of the polymer.

Curing agents are not used in thermoplastic adhesive compositions. The adhesive composition applied to the surface to be bonded in a viscous liquid state hardens when cooled and bonds the surfaces. Thermoplastic synthetic adhesives have flexibility and, in most cases, relatively low heat resistance.

Thermo-reactive synthetic adhesives can be single or multi-component. Thermo-reactive adhesives are used in the preparation of metal and non-metal constructions due to their high adhesion and heat resistance [1]. Mostly, epoxy adhesives consist of epoxy resins and curing agents. It can be in one-component or two-component packaging, depending on the applied curing method and the curing agent. The epoxy adhesive which hardens at room temperature, the curing agent and epoxy resin are packaged separately. It hardens quickly when mixed during use. In one-component epoxy adhesives, the curing agent and the epoxy resin are packaged together and hardened at high temperatures during use[2]. Therefore, these glues should be kept at a low temperature. Curing can occur by adding curing agents due to the interaction of reactive units of oligomers or the effect of heat, ultraviolet rays, high-energy radiation, and catalysts [3].

Synthesis of allyl propionate-styrene-maleic anhydride ternary copolymer

The allyl phenyl ether-styrene-maleic anhydride ternary copolymer used for the preparation of adhesive composition was obtained by radical copolymerization of allyl propionate (APr), styrene (St), and maleic anhydride (MA) in butyl acetate solution with the presence of azobisisobutyronitrile (AIBN) [4]. The calculated amount ([MA]:[APr]:[St]=2:1:1) of maleic anhydride, allyl phenyl ether, styrene, and initiator is transferred to ampoule by dissolving in butyl acetate in a beaker and placed in a thermostat with the temperature of 80 ^{o}C. After a certain time, the ampoule is removed from the thermostat. The mixture is poured into a beaker and the copolymer is precipitated with technical alcohol. Then it is washed 2-3 times with the precipitant, filtered in a Buchner funnel, and dried in a vacuum-drying cabinet at 40^{o}C.

Preparation of adhesive composition

For the preparation of adhesive composition, the ternary copolymer is first crushed well in a porcelain bowl and turned into powder. Ternary copolymer weighed to the nearest 0.1 g and a calculated amount of ED-20 epoxy resin was added to the porcelain bowl and mixed. The mixture which is in the form of a paste under normal conditions is kept for 30 minutes in a thermostat with a temperature of 70-80^{o}C with occasional stirring. At this time, the copolymer dissolves in the epoxy resin and a clear viscous liquid is obtained. If the temperature in the thermostat is high or the time the mixture stays in the thermostat is long, then the formation of gel is observed and it is not possible to prepare a disk from the mixture for studying adhesive or dielectric properties. According to the methodology mentioned above, 100 k.h. ED-20 brand epoxy resin and 10, 15, 20, 25, 30 k.h. The APr-MA-St adhesive composition was prepared based on a ternary copolymer was prepared and the effect of various factors on the properties of this composition was studied.

Determination of some physical and physicochemical properties of adhesive composition

Freshly prepared adhesive composition is used to determine the appearance of high-resistance liquid adhesives. The prepared adhesive composition is mixed in a glass or porcelain bowl with a capacity of 50-100 cm^3. With a clean, dry glass rod, the adhesive is lifted 10-20 cm above the glass and the flowing adhesive strip is observed to be homogeneous without any extraneous mixture.

Duralumin plates were used to determine the sliding fracture resistance limit of the adhesive. The value of sliding fracture resistance in the crushing machine of duralumin plates glued and cured at temperatures of 140, 160, and 180°C for 2 hours was determined. During the curing of the adhesive composition prepared in the ratio of ED-20:CP=100:25 at temperatures of 140, 160, and 180°C for 2 hours, the sliding fracture resistances for duralumin plates were 13.8, 13.9, and 14.4 MPa, respectively.

The tensile fracture resistance of the adhesive composition is based on 100 k.h. ED-20 epoxy resin and 25 m.f. allyl propionate-styrene-maleic anhydride ternary copolymer was determined. The prepared adhesive composition was poured into a special mold and cured at a temperature of 180°C. As a result of curing, a smooth, non-porous, 150 mm long, 20 mm wide, and 2 mm thick sample was prepared. The ends of the prepared sample were cured in a crushing machine and stretched under the influence of load. Then, by dividing the value of the load obtained according to the scale by the value of the working area, the value of tensile fracture resistance was obtained as 2.13 MPa.

The angular tangent of dielectric loss and dielectric conductivity for a disk-shaped sample made on the basis of ED-20 epoxide resin and allyl propionate-styrene-maleic anhydride ternary copolymer was determined for a current with a frequency of 106 Hz.

The results of the measurements, dielectric permeability, and dielectric loss value for the cured adhesive composition are given below:

Table 1. Dielectric properties

d_{mm}	C_1	C_2	ΔC	Q_1	Q_2	ΔQ	$Tg\delta$	ε
1,5	100	80	20	190	70	120	$45 \cdot 10^3$	1,8

The degree of swelling (α%) of the compositions cured and prepared in different mass ratios in different solvents was determined and the results are given in the table below:

Table 2. The degree of swelling of the cured composition in different solvents

Solvents	The swelling rate for compositions prepared in different mass ratios, α%.				
	100:30	100:25	100:20	100:15	100:10
Toluene	0.22	0.63	4.45	37.45	-4.46
Chlorbenzol	0.10	0.67	21.32	27.77	-13.6
1,4-dioxane	0.24	0.75	3.85	26.84	-4.99
Butyl acetate	3.21	4.09	5.38	35.82	-6.4
Hexsane	0.66	1.5	2.0	3.33	4.6
Carbon 4-chloride	2.51	3.9	5.26	15.39	-3.5
Acetone	-2.6	-3.27	-14.01	-14.93	-19.3

Result

At first, the yield of the ternary copolymer synthesized in optimal conditions was 75.4% and the characteristic viscosity was -0.65-0.68 dl/g. Adhesive compositions were prepared in different proportions of allyl propionate-styrene-maleic anhydride ternary copolymer and ED-20 epoxy resin. The curing of ED-20 epoxy resin and copolymer was studied and the influence of the

temperature and the amount of copolymer on the curing process was determined. The property of bonding duralumin plates of the glue obtained by curing under different conditions was studied. It was determined that the sliding fracture resistance of the adhesive compositions prepared in different mass ratios of the copolymer and ED-20 epoxy resin for duralumin plates was higher in the ED-20:CP=100:25 ratio. The tensile fracture resistance and dielectric properties of the adhesive composition prepared in the ratio of ED-20:CP =100:25 were determined. The obtained results show that these materials have good electrical insulation properties. The degree of swelling of the adhesive compositions prepared by curing in different mass ratios in different solvents was determined. From the obtained results, it is known that as the mass amount of copolymer in the adhesive composition decreases, the degree of swelling in solvents increases.

References

1. Cyprien Gay. Some fundamentals of adhesion in synthetic adhesives, - 2003, pp. 1–2.
2. Kablov, E.N., Chursova, L.V., Lukina, N.F. et al. A study of epoxide–polysulfone polymer systems for high-strength adhesives of aviation purpose. // Polym. Sci. Ser. – 2017, D 10, pp. 225–229. https://doi.org/10.1134/S1995421217030066
3. Chunfu Chen, Bin Li, Masao Kanari and Daoqiang Lu. Epoxy Adhesives. Chapter Metrics Overview, - 2019, pp.6-8.
4. O.H.Əkbərov, R.E. Məmmədova, E.O.Əkbərov. Okten-1-malein anhidridi-stirol üçlü birgə polimerinin sintezi və tədqiqi. // Kimya problemləri. – 2007, №3, p. 10.
5. Kochergin, Y.S., Pyrikov, A.V., Kulik, T.A. et al. Investigation of epoxide adhesive compositions cured with polyoxypropylene triamine. // Polym. Sci. Ser. – 2010, D 3, pp. 47–49. https://doi.org/10.1134/S1995421210010077
6. Petrova, A.P., Lukina, N.F., Dement'eva, L.A. et al. Film structural adhesives. // Polym. Sci. Ser. – 2015, D 8, pp. 138–143. https://doi.org/10.1134/S1995421215020148
7. Fedoseev, M., Gurina, M., Sdobnov, V. and Kondyurin, A. Study of the Reaction of Epoxides with Carboxylic Acids by IR and Raman Spectrometry. // J. Raman Spectrosc., - 1996, 27: pp. 413-418. https://doi.org/10.1002/(SICI)1097-4555(199605)27:5<413::AID-JRS947>3.0.CO;2-T
8. Vyatkina, M.A., Gorbatkina, Y.A., Gorbunova, I.Y. et al. Effect of Oligomeric Copolyimides on the Properties of Epoxy Binders. // Mech Compos Mater. – 2023, 58, pp. 857–866. https://doi.org/10.1007/s11029-023-10074-1
9. Konoplin, A.Y., Baurova, N.I. Thermogravimetric Analysis of a Weld-Bonded Joint with Various Types of Adhesive Materials. // Polym. Sci. Ser., - 2022, D 15, pp. 166–170. https://doi.org/10.1134/S1995421222020125
10. Gur'eva, L.L., Kuzub, L.I., Tarasov, A.E. et al. Epoxy Nanocomposites Containing Silver Nanoparticles with Oligostyrylcarboxylate Ligands. // Polym. Sci. Ser. – 2022, B 64, pp. 209–218. https://doi.org/10.1134/S1560090422020105
11. Sirotin, I.S., Son, V.X., Gorbunova, E.A. et al. The Composition and Some Properties of Epoxy Oligomers Based on Hexachlorocyclotriphosphazene and Diphenylolpropane. // Polym. Sci. Ser., - 2022, D 15, pp. 457–463. https://doi.org/10.1134/S1995421222030261
12. G. Fantin et al., "Functionalization of poly(organophosphazenes)—III. Synthesis of phosphazene materials containing carbon-carbon double bonds and epoxide groups," // Eur. Polym. J. – 1993, 29, pp. 1571–1579.

ALLİL PROPİONAT-STİROL-MALEİN ANHİDRİD ÜÇLÜ SOPOLİMERİ ƏSASINDA YAPIŞQAN KOMPOZİSİYASININ HAZIRLANMASI

Fariz Əmirli[1], Rəsmiyyə Məmmədova[2], Aman Eyvazov[3]

[1,2,3]Azərbaycan Dövlət Neft və Sənaye Universiteti, Bakı, Azərbaycan
[1] fariz.emirov@asoiu.edu.az, http://orcid.org/0000-0002-9095-2982
[2] rasmiyyamammadova76@gmail.com, http://orcid.org/0009-0007-8698-8302
[3] aman.eyvazov@mail.ru, http://orcid.org/0009-0007-0318-1029

XÜLASƏ

Allil propionat-stirol-malein anhidrid üçlü sopolimer və ED-20 epoksid qatranı əsasında yapışqan kompozisiyalar hazırlanmış və bu yapışqan kompozisiyaların bəzi fiziki və fiziki-kimyəvi xassələri müəyyən edilmişdir. Yapışqan kompozisiyalar müxtəlif nisbətlərdə allil propionat-stirol-malein anhidrid üçlü sopolimer və ED-20 epoksid qatranından (100 k.h. ED-20 epoksid qatranı üçün 10, 15, 20, 25, 30 k.h. sopolimer) hazırlanmışdır. Müxtəlif şəraitdə qaynar bərkimə yolu ilə alınan yapışqanın duralüminium lövhələrinin yapışdırılma xüsusiyyəti öyrənilmişdir. Müəyyən edilmişdir ki, duralumin lövhələr üçün sopolimer və ED-20 epoksid qatranının müxtəlif kütlə nisbətlərində hazırlanmış yapışdırıcı kompozisiyaların sürüşmədə qırılma müqaviməti ED-20:CP=100:25 nisbətində daha yüksək olmuşdur. Bu kütlə nisbətində əldə edilən yapışqan tərkibi 140, 160 və 180 ^{o}C-də 2 saat quruduqda duralüminium lövhələr üçün sürüşmədə qırılma müqaviməti 13,8, 13,9 və 14,4 MPa olmuşdur. ED-20:CP=100:25 nisbətində hazırlanmış yapışqan tərkibinin dartılmada qırılma müqaviməti və dielektrik xüsusiyyətləri müəyyən edilmişdir. Bu nisbətdə hazırlanmış yapışqan tərkibinin dartılmada qırılma müqaviməti 2,13 MPa, dielektrik keçiriciliyi 1,8 (106 Hs tezlikdə) və dielektrik itkisinin bucaq tangensi 45·10-3 (106 Hs tezliyində) olmuşdur.). Müxtəlif həlledicilərdə müxtəlif kütlə nisbətlərində bərkidilməklə hazırlanan yapışdırıcı kompozisiyaların şişmə dərəcəsi müəyyən edilmişdir. Toluol, xlorbenzol, 1,4-dioksan və butilasetatda 100:25 kütlə nisbətində sərtləşmə yolu ilə hazırlanan yapışqan tərkibinin şişkinlik dərəcələri müvafiq olaraq 0,63, 0,67, 0,75 və 4,19% təşkil edir.

Açar sözlər: allil propionat, stirol, malein anhidrid, üçlü sopolimer, epoksid qatranı, yapışqan kompozisiyası, şişmə dərəcəsi, dielektrik keçiricilik.

ПРИГОТОВЛЕНИЕ КЛЕЙНОЙ КОМПОЗИЦИИ НА ОСНОВЕ ТРОЙНОГО СОПОЛИМЕРА АЛЛИЛПРОПИОНАТ-СТИРОЛ-МАЛЕИНОВЫЙ АНГИДРИД

Фариз Амирли[1], Расмия Мамедова[2], Аман Эйвазов[3]

[1,2,] Азербайджанский Государственный Университет Нефти и Промышленности, Baku, Azerbaijan
[1] fariz.emirov@asoiu.edu.az, http://orcid.org/0000-0002-9095-2982
[2] rasmiyyamammadova76@gmail.com, http://orcid.org/0009-0007-8698-8302
[3] aman.eyvazov@mail.ru, http://orcid.org/0009-0007-0318-1029

РЕЗЮМЕ

Получены клеевые композиции на основе тройного сополимера аллилпропионата, стирола и малеинового ангидрида и эпоксидной смолы ЭД-20 и определены некоторые физические и физико-химические свойства этих клеевых композиций.

Клеевые композиции готовили в различных соотношениях тройного сополимера аллилпропионат-стирол-малеиновый ангидрид и эпоксидной смолы ЭД-20 (сополимер 10,15, 20, 25, 30 м.ч. на 100 м.ч. эпоксидной смолы ЭД-20).

Изучено свойство склеивания дюралевых пластин клеем, полученным отверждением в различных условиях. Установлено, что сопротивление разрушению при скольжении клеевых композиций, приготовленных в различных массовых соотношениях сополимера и эпоксидной смолы ЭД-20 для дюралевых плит, выше при соотношении ЭД-20:ЦП=100:25. При отверждении клеевой композиции, полученной в данном массовом соотношении, при температуре 140, 160 и 180 ^{o}C в течение 2 часов сопротивление разрушению при скольжении дюралюминиевых пластин составило 13,8, 13,9 и 14,4 МПа.

Определены сопротивление разрушению при растяжении и диэлектрические свойства клеевой композиции, приготовленной в соотношении ЭД-20:ЦП=100:25. Сопротивление разрушению клеевой композиции, приготовленной в этом соотношении, составило 2,13 МПа, диэлектрическая проницаемость - 1,8 (на частоте 106 Гс) и угловой тангенс диэлектрических потерь - 45·10-3 (на частоте 106 Гс).). Определена степень набухания клеевых композиций, приготовленных отверждением в различных массовых соотношениях в разных растворителях. Степени набухания клеевой композиции, приготовленной отверждением в массовом соотношении 100:25 в толуоле, хлорбензоле, 1,4-диоксане и бутилацетате, составляют 0,63, 0,67, 0,75 и 4,19% соответственно.

Ключевые слова: аллилпропионат, стирол, малеиновый ангидрид, тройной сополимер, эпоксидная смола, клеевой состав, степень набухания, диэлектрическая проводимость.