ISSN 1027-5495. Functional Materials, 27, No.3 (2020), p. 522-525.
doi:https://doi.org/10.15407/fm27.03.522

Study on residual stresses in epoxy composites with disperse fillers caused by the parameters of external surface layers

I.G.Dobrotvor, D.P.Stukhlyak, A.G.Mykytyshyn, V.R.Kobelnyk

Ternopil Ivan Puluj National Technical University,
56 Ruska Str., 46001 Ternopil, Ukraine

Received September 4, 2019

The influence of transition zones in the "epoxy binding — filler" system on the residual stresses when changing thickness of the coatings has been investigated. In the composites, disperse fillers with different physical nature and activity to the polymer matrix were used.

Keywords: epoxy binder, matrix, external surface layers, residual stresses, coatings.

Дослідження залишкових напружень дисперснонаповнених епоксикомпозитів параметрами зовнішніх поверхневих шарів. *І.Г.Добротвор, Д.П.Стухляк, А.Г.Микитишин, В.Р.Кобельник.*

Досліджено вплив перехідних зон у системі "епоксидний зв'язувач — наповнювач" на залишкові напруження з урахуванням товщини покриттів. У композитах використано дисперсні наповнювачі різної фізичної природи та активності у відношенні до полімерної матриці.

Исследовано влияние переходных зон в системе "эпоксидное связующее — наполнитель" на остаточные напряжения с учетом толщины покрытий. В композитах использованы дисперсные наполнители различной физической природы и активности по отношению к полимерной матрице.

1. Introduction

Epoxy composite polymers and their derived composite materials provide the necessary set of physical and mechanical properties, and operational characteristics. Their derived composites are used as coatings of component surfaces in mechanisms and machines. The formation of such materials is effective when disperse fillers of different nature are added. The effect of a filler on polymer properties is defined by different factors: the chemical nature of a polymer and a filler, the nature of a filler surface, the size and the shape of particles, their ability to form own structures, the flexibility change of macromolecules and the structure of the polymer. It is known that residual stresses occur during the formation of such materials, depending on the filler amount and the coating thickness. Their values are significantly affected by the processes which occur at the breaking point of phase separation in the "epoxy matrix — disperse filler" system. In this case such an area is characterized by the volume of external surface layers (ESL) and the degree of binding cross-linking in them. Therefore the use of ESL study results to determine the correlation dependence with residual stresses is effective in the formation of new composite materials [1–3].

The subject of the research is ED-20 epoxy-diane oligomer (ASTM D 1726, DER-332) which is characterized by insignificant shrinkage effect, high adhesive and cohesive durability, adaptability during the application on lengthy surfaces of complex profile, and advanced raw material base. The majority of such materials formed on the basis of epoxy binding are used as coatings. Taking into account their formation conditions, the polyethylene polyamine curative (PEPA) is used for the epoxy binding cross-linking, which enables the formation of coatings from composites at room temperature.

The purpose of the studies is the evaluation of composite residual stresses dependences on the coating thickness and the degree of material filling with disperse fillers. The information on the interphase interaction of binding macromolecules with active centres on the surface of the mineral filler during the material formation is important. It is important to determine the effect of this interaction on the properties of epoxy composite materials during their formation and operation. It is important to study the formation processes of transition areas of the interphase interaction between the filler and binding materials, which properties differ from the matrix properties in the binding volume. The typical studies of such areas are described by the parameters of external surface layers (ESL). By managing the ESL object, you can intentionally adjust the properties of the material during its formation [2, 3]. It should be noted that the material in the separation area differs from the material in the matrix volume in terms of structure and properties (including optical). In most cases, the properties of such areas determine the properties of the material as a whole. The degree of cross-linking in the external surface layers also significantly affects the residual stresses and adhesion strength of epoxy composite materials and determines their physical and mechanical properties, including residual stresses. The research results will make it possible to form materials and coatings with specified performance characteristics [4, 5].

2. Experimental

The composites were prepared by the hydrodynamic combining of the matrix components (ED-20 epoxy resin) and disperse fillers (aluminium and copper oxides, ferrite with effective particle diameter of 63 μm and brown slime with effective particle diameter of 40–60 μm). Further the components were combined for 5 min with the addition of a hardener (PEPA). Residual stresses in the coatings were determined depending on the nature and content of fillers using the cantilever method according to ASTM D 7264/D7264M-07, ASTM D 790. The coating was formed on a substrate made of carbon steel of ordinary quality (Steel 3) with the thickness $\delta = 0.3$ mm. This steel is used for irresponsible parts, with the requirements of high ductility, low-load elements, which are operated at constant loads and positive temperatures.

3. Results and discussion

The results on residual stresses are given in Table 1.

Simultaneous estimations on the ESL volume and density were performed for each composite material (CM) with different filler concentration. The results of the previous estimations of ESL thickness around the grains of a disperse filler were used in these studies [4]. To determine the redundant mass (Δm) in a volume unit of interphase interaction areas around the grains of the fillers, an equation was solved:

$$\Delta m + (1 - z(q)/100) \cdot \nu_o \cdot \rho_o + nz(q) \cdot \rho_z = q + q_0, \quad (1)$$

where $z(q)$ is the percentage composition of the oligomer which passed into ESL state, $nz(q)$ is the amount of filler particles in the volume unit of the material, q is the filler content in the material, q_0 is the oligomer content, ν_o is the oligomer volume, ρ_o is the

Table 1. Residual stresses in composites with different filler content, $\sigma_з$, MPa

Filler	Filler content, q, pts. wt. per 100 pts. wt. of the binding							
	0	10	20	40	60	80	100	120
Red slime	7.2	5.3	3.3	3.0	4.5	3.7	3.6	2.7
Ferrite	7.2	6.5	5.8	4.9	5.1	5.5	4.6	4.2
Copper oxide	7.2	5.0	3.4	2.8	4.1	3.7	5.3	5.1
Aluminium oxide	7.2	6.4	5.5	4.8	5.2	5.0	4.1	4.0

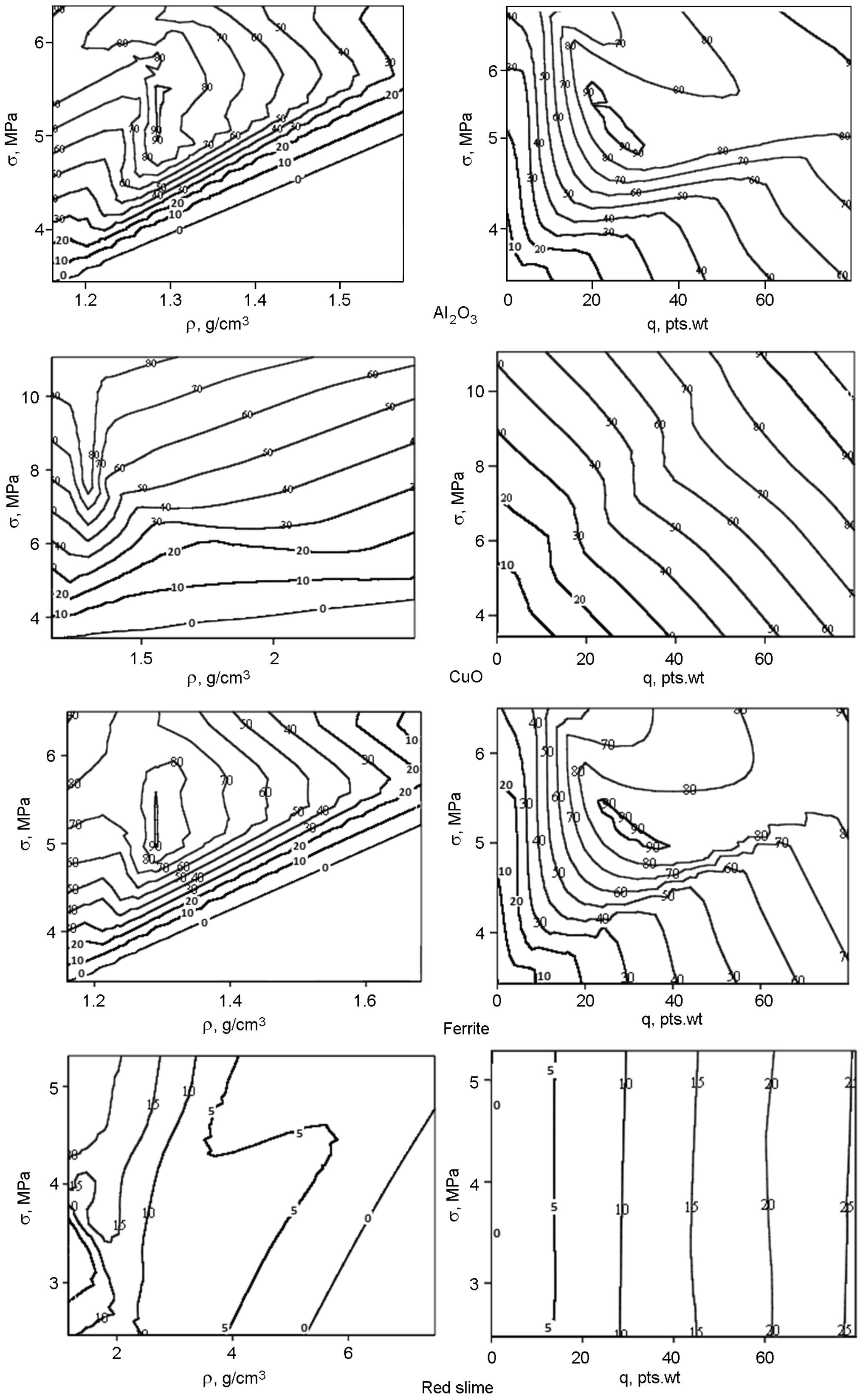

Fig. Diagram dependences of ESL extensions on residual stresses (σ, MPa) of epoxy composites, ESL percentage composition (z, %) in the material, ESL density (ρ, g/cm^3) and filler concentrations (q, pts. wt.) for aluminium oxide (Al_2O_3), copper oxide (CuO), ferrite and red slime.

Table 2. ESL densities of composites with different filler content

Filler material	CM density, ρ_c, g/cm^3							
	0	5	10	20	30	50	80	100
Ferrite	0.970	1.061	1.136	1.142	1.155	1.155	1.371	1.482
Red slime	0.970	1.072	1.13	1.135	1.142	1.151	1.392	1.499
Copper oxide	0.970	1.139	1.158	1.224	1.303	1.365	1.431	1.495
Aluminium oxide	0.970	1.055	1.136	1.144	1.150	1.163	1.298	1.358

oligomer density, ρ_z is the density of the material of the filler grains (particles).

The evaluations for each filler provided $\Delta m = 0.118$ g/cm^3, which indicates the independency of this characteristic from the ESL structure and the filler nature. The ESL density (Table 2) was determined by the formula:

$$\rho(q) = \frac{100 \cdot \Delta m}{z(q)} + \rho_o. \tag{2}$$

The results on the residual stresses were obtained for epoxy composites containing fillers with the dispersity of 63 μm and 40–60 μm in different concentrations (q) (in pts. wt. of the filler per 100 pts. wt. of oligomer). Also the ESL percentage composition, as a demonstration of interphase interaction areas, and the ESL density for different filler contents were evaluated. This made it possible to construct four-factor diagrams of matrix states of a cross-linked composite for fillers of different nature (Fig.).

The analysis of the diagram indicates that the filler content in the protective coating material significantly affects the residual stresses which, in their turn, affect the cohesive durability of CM. However, such dependence can in no case be linear or algebraic. The constructed 4-dimensional diagrams make it possible to trace the smoothed dependences of the percentage of LPG on the filler content, composite density and residual stresses. The nature of these dependences demonstrates a significant affinity of their nature from the nature of the fillers and its content in the composite (Fig.). The topology of the level lines, in particular for oxides, and their similarity makes it possible to assert about similar diagrams for fillers of similar nature not given in this paper. In a more general interpretation, it can be argued that in the filler content range for the coating material: 30...80 pts. wt. per 100 pts. wt. of oligomer, a CM structure is formed with significant residual stresses in the epoxy matrix, thus with a high degree of cross-linking in the whole range of studied coating thicknesses. Given that, low values of residual stresses confirm the plasticizing effect of the specified filler during the formation of the material. This is manifested in the uniform distribution of filler particles in the material the subsequent formation of ESL of considerable length [6].

4. Conclusions

The obtained diagrams make it possible to select the content and composition of fillers in order to improve the production technologies of composites with pre-specified physical and mechanical properties. It should be noted that the most effective way to prevent corrosion is to use polymer composite protective coatings in chemical, oil processing and food industry.

References

1. S.G.Garnier, in: Proc. Intern. Seminar Organized by Deutsche Forschungsanstalt fur Luft- und Raumfahrt, Koln, 126 (1991), p.165.
2. V.V.Yanovsky, M.I.Kopp, M.A.Ratner, *Functional Materials*, **26**, 131 (2019).
3. R.F.Gibson, *Composite Structures*, **12**, 92 (2010).
4. P.Stukhlyak, I.Dobrotvor, M.Mytnyk, A.Mykytyshyn, *Przetw. Tworzyw. Polymer Proc.*, **1**, 23 (2017).
5. I.G.Dobrotvor, P.D.Stukhljak, A.G.Mykytyshyn, M.M.Mytnyk, Analysis of Composite Pattern Image Recognition Systems, Ivan Pulyuy Ternopil National Technical University, Ternopil (2018).
6. U.Ruiz, P.Pagliusi, C.Provenzano et al., *Adv. Funct. Mater.*, **14**, 22 (2012).