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COMPOSITES THEORY AND PRACTICE

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CHARPY IMPACT TESTS OF EPOXY MATRIX FILLED WITH POLY(UREA-FORMALDEHYDE) MICROCAPSULES FOR SELF-HEALING APPLICATIONS

Smart self-healing epoxides have attracted immense interest in the industry due to their capability to prevent crack propagation and increase material service life. Self-healing can be achieved via a number of approaches, where microcapsule-based systems are deemed to be the closest to market implementation. The work presented here demonstrates the effect of polymeric microcapsules made of poly(urea-formaldehyde) on the Charpy impact resistance of a standard epoxy matrix. Poly(urea-formaldehyde) microcapsules containing epoxy resin (EPIDIAN 52) and organic solvent (Ethyl phenylacetate) were prepared using in-situ polymerisation in an oil-in-water emulsion as described in the literature. The Charpy impact tests were performed on specimens made of neat epoxy resin (EPIDIAN 52) - amine hardener (Z1) as well as for the epoxy filled with microcapsules with 1, 2.5, 5, 10 and 25 wt.%. The test results have shown that the presence of brittle and spherical additives has a detrimental effect on the mechanical properties of the polymer, resulting in a maximum 80% reduction in impact strength for the samples with the highest content of microcapsules. In addition, the fracture surfaces of the impacted specimens were investigated using a Scanning Electron Microscope (SEM). Significant differences were observed between the reference samples and those containing microcapsules, particularly when the microcapsule weight fraction is high.

Keywords: epoxy resin, microcapsules, composites, Charpy impact, scanning electron microscopy

BADANIA UDARNOŚCI KOMPOZYTÓW O OSNOWIE EPOKSYDOWEJ ZAWIERAJĄCEJ MIKROKAPSUŁKI MOCZNIKOWO-FORMALDEHYDOWE DO ZASTOSOWAŃ W MATERIAŁACH SAMONAPRAWIALNYCH

Polimery epoksydowe zdolne do samonaprawiania cieszą się dużym zainteresowaniem przemysłu dzięki ich zdolnościom do hamowania propagacji pęknięć, przez co wydłużają żywotność materiału w trakcie jego eksploatacji. Zdolność polimeru do samonaprawiania może być osiągnięta w różny sposób. Spośród różnych systemów samonaprawiania wykorzystanie mikrokapsułek wydaje się być najbliższe możliwości ich praktycznego zastosowania w przemyśle. W niniejszej pracy zbadano wpływ polimerowych mikrokapsułek wykonanych z poli(moczniko-formaldehydu) na odporność udarową standardowej żywicy epoksydowej, mierzoną metodą Charpy'ego. Poli(mocznikowo-formaldehydowe) mikrokapsułki zawierające żywicę epoksydową (EPIDIAN 52) oraz rozpuszczalnik organiczny (etylofenylooctan) zostały wytworzone metodą polimeryzacji w wodnej emulsji znanej z literatury. Udarność metodą Charpy'ego została zbadana dla żywicy epoksydowej (EPIDIAN 52) utwardzanej aminowym utwardzaczem (Z1) bez i z zawartością 1, 2,5, 5, 10 i 25% wagowych mikrokapsułek. Wykonane badania wykazały, że obecność kruchych i sferycznych dodatków ma niekorzystny wpływ na właściwości mechaniczne polimeru, powodując maksymalnie 80% spadek udarności dla próbek o najwyższej zawartości mikrokapsułek. Ponadto kruche przełomy zostały poddane obserwacjom mikroskopowym za pomocą skaningowej mikroskopii elektronowej (SEM). Stwierdzono znaczące różnice pomiędzy próbkami referencyjnymi a modyfikowanymi mikrokapsułkami, w szczególności przy dużej zawartości mikrokapsułek.

Słowa kluczowe: żywica epoksydowa, mikrokapsułki, kompozyty, udarność Charpy'ego, skaningowa mikroskopia elektronowa

INTRODUCTION

Epoxy polymers are widely used in a number of applications including adhesives, coatings, electronics, and composites as they exhibit excellent mechanical, chemical and thermal properties. Depending on their application and desired properties, a number of epoxy pre-polymers, hardeners and additives are available to formulate the polymer. The diglycidyl ether of bisphenol A (DGEBA) and tetraglycidyl methylenedianiline (TGMDA) combined with amine, phenols, anhydrides, polyphenols and polysulfides are by far the most common constituents [1-3]. However, epoxides are brittle in nature, which makes them susceptible to damage induced by high service loadings and harsh environmental conditions. Nowadays, costly and time-consuming

damage detection and manual repairs are the most common strategies addressing the problem. Self-healing offers an additional paradigm to increase the material service life and its reliability. There are three conceptual approaches developed to date, including microcapsules containing the reaction chemicals incorporated in the polymer, vascular networks distributing healing chemistries within the material, and inherently reversible bonding in the polymer [3-5]. Microcapsule based approaches are considered the most commercially viable as they do not affect the chemical composition of the base material, are easily prepared by a number of techniques and can be used as a simple additive to the polymer [4, 5].

There is a number of particulate fillers that have been used in epoxy resins and include aluminium, calcium carbonate, copper, colloidal silica, hollow glass beads, etc. [1, 2]. By utilizing such fillers, a number of properties may be improved, including thermal characteristics, shrinkage, electrical conductivity, viscosity, and toughness. A number of parameters should be considered before applying additives, including particle size, surface chemistry, and volume fraction. However, the presence of microspheres such as hollow glass, rubber, core-shell particles, thermoplastics, etc., may result in a reduction in their mechanical properties [6]. Huang et al. [7] reported that the presence of 10% hollow glass spheres in a polyester matrix results in a 32% decrease in the Young's modulus, and is dependent on the volume fraction of the filler. In contrast, many reports describe an increase in material fracture toughness using particulate fillers [8, 9]. It has been demonstrated in literature that incorporating only 1% hollow glass spheres results in a 16% increase in the stress intensity factor (K_{IC}) measured for a standard epoxy resin [10].

Many authors have investigated the effect of polymeric microcapsules made of poly(urea-formaldehyde) on the tensile and fracture properties of bulk epoxy-based polymers [11-14]. Incorporating the spherical filler resulted in a maximum 50% decrease in the Young's modulus and an increase of about 30% in the polymer fracture toughness (K_{IC}). Both of the properties depend greatly on the size and the loading of the embedded microcapsules in the material. In other studies, it has been demonstrated that the inclusion of microcapsules results in fatigue life extension and a reduction in fatigue crack growth in epoxy resins [15, 16]. Moreover, polymeric microcapsules used in self-healing studies, along with a Grubbs' catalyst, were reported to increase fracture toughness and fatigue life in self-healing adhesives. When highly concentrated in the region of crack propagation, healing components caused a substantial decrease in the fracture properties [17, 18].

However, there is no comprehensive published work on the effects associated with the presence of microcapsules on the impact resistance. In this work, the effect of polymeric microcapsules made of poly(urea-formaldehyde) on the Charpy impact properties in an epoxy resin is determined. Poly(urea-formaldehyde) microcapsules were embedded in a commercially sourced epoxy resin at various weight fractions. The microcapsules were first prepared using the in-situ polymerization of urea and formaldehyde in an oil-in-water emulsion as described in the literature [19, 20]. The resulting microcapsules were then uniformly dispersed in an EPIDIAN 52 resin and consolidated with an amine hardener Z1 at 60°C for 24 hours and post cured at 80°C for 2 hours. The EPIDIAN 52 and Z1 composition is often used as adhesives, coatings and matrix phases in fiber reinforced composites. Poly(urea-formaldehyde) microcapsules were used as they exhibit high thermal stability and good adhesion to epoxy resins. These capsules were often used in the literature [20] to deliver liquid phase healing agents into the crack environment. Charpy impact tests were performed on samples containing 1, 2.5, 5, 10 and 25 wt.% of capsules and compared to neat epoxy resin containing no additives. The collected data show that the presence of microcapsules has a negative impact on the structure, resulting in a maximum 80% decrease in the impact resistance. Additionally, scanning electron microscopy (SEM) was used to analyze the surface morphology of the fractured samples. The microscopic analysis revealed features characteristic of fractured epoxy polymers during impact and indicated changes in the crack propagation mechanism with an increasing loading percentage of microcapsules.

EXPERIMENTAL PROCEDURE

Poly(urea-formaldehyde) microcapsules were used in the study as the additive for the epoxy resin. The microcapsules were prepared using standard in-situ polymerization in an oil-in-water emulsion described in the literature [19]. For purposes of the work, the microcapsules here were filled with a mixture of epoxy resin (EPIDIAN 52) or organic solvent facilitating microencapsulation (Ethyl phenylacetate). After synthesis, the particle size was measured using a scanning electron microscope (SEM) and processed using ImageJ software.

The test samples were prepared using a commercially sourced epoxy resin (EPIDIAN 52) and amine hardener Z1 (100:13 pph ratio). A number of composites containing the spherical additive were prepared by mixing 1, 2.5, 5, 10 and 25 wt.% of microcapsules with the epoxy resin and then with the desired amount of hardener. In addition, samples containing only neat epoxy resin were also prepared as the reference. After mixing with the hardener, the resin was degassed at room temperature for 15 minutes and poured into silicone molds with the desired dimensions. The epoxy resin was then consolidated in accordance to the manufacturer's recommendations at 60°C for 24 hours and post cured at 80°C for 2 hours.

The prepared samples were impacted in a RESIL 5.5 pendulum impact tester with Charpy configuration. All the results were obtained using a standard 15J hammer. A minimum of 5 samples for each variable was tested. The tests were performed in accordance to PN-EN ISO 179-1 [21]. Scanning electron microscopy was used to analyze the fracture surfaces, using a HITACHI TM 3000 desktop SEM microscope. The specimens were first put onto a conductive stub and sputter coated with a 16 nm layer of Ag/Pt prior to observation.

RESULTS AND DISCUSSION

Size distribution and microstructure of microcapsules

Figure 1 illustrates the SEM micrographs of the poly(urea-formaldehyde) microcapsules filled with epoxy resin-organic solvent used as the additive in the work. The size distribution of the microcapsules was determined for at least 500 section length measurements using ImageJ and ranges from 10 to 170 μm. Figure 1b shows a single microcapsule with a rough exterior shell wall made of the growing polymer in the emulsion. The rough surface is beneficial due to increased surface area and enhanced surface adhesion [19, 22].

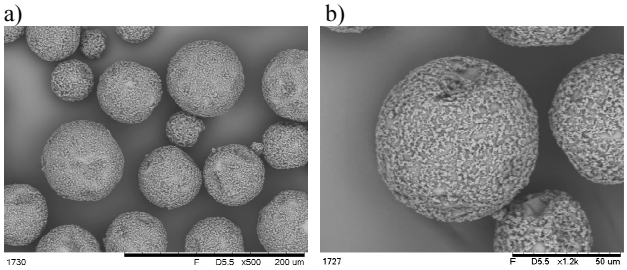

Fig. 1. Poly(urea-formaldehyde) microcapsules prepared using *in-situ* polymerisation of urea and formaldehyde in oil-in-water emulsion

Rys. 1. Zdjęcie SEM mikrokapsułek mocznikowo-formaldehydowych wytworzonych z zastosowaniem polimeryzacji *in situ* mocznika i formaldehydu w wodno-olejowej emulsji

Charpy impact tests

Figure 2 shows the Charpy impact test results of the epoxy filled with poly(urea-formaldehyde) microcapsules at various weight fractions. Table 1 summarizes the collected results for the impact energy and Charpy impact resistance.

By analyzing the data, it is clear that the presence of the polymeric microcapsules has a detrimental effect on Charpy impact resistance of the epoxy. The epoxy resin with the addition of 1 wt.% microcapsules has a 66% reduced impact strength when compared to the reference sample containing only neat resin. At higher weight loading percentages, ranging from 2.5 to 25 wt.% of the additive, there is an average 80% reduction in the impact resistance, which is independent of the microcapsule loading percentage in the polymer.

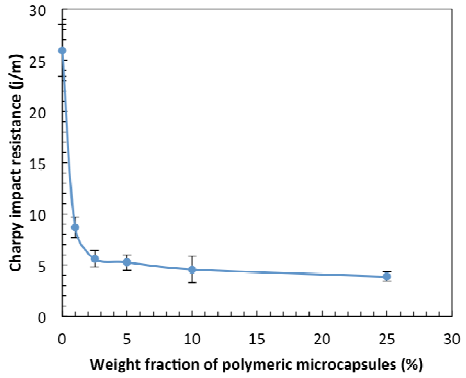

Fig. 2. Charpy impact resistance as a function of microcapsule weight fraction

Rys. 2. Wyniki udarności Charpy'ego w funkcji frakcji wagowej mikrokapsułek

TABLE 1. **Charpy impact resistance of epoxy matrix filled with microcapsules at various weight fractions**

TABELA 1. **Wyniki udarności Charpy'ego kompozytów o osnowie epoksydowej zawierającej mikrokapsułki o różnych frakcjach wagowych**

Sample	Wt.% of microcapsules	Impact energy [J]	Impact resistance [J/cm^3]
Ref	0	0.428	25.9 ±2.5
ST-1	1	0.144	8.7 ±1.0
ST-2.5	2.5	0.0876	5.6 ±0.8
ST-5	5	0.0822	5.2 ±0.8
ST-10	10	0.069	4.7 ±1.3
ST-25	25	0.057	3.8 ±0.5

Scanning electron microscopy

The most promising samples after the impact tests were chosen for the microscopic analysis. The samples were gold palladium sputter coated and examined using a scanning electron microscope (SEM). Figure 3 shows the cross section of neat epoxy resin after the test. The smooth area at the center and the propagating marks indicate the impact point. It also indicates that a single crack was responsible for the rupture. The irregular fracture surface suggests crack arrest and the direction of crack propagation. The fracture surfaces for specimens containing microcapsules are presented in Figure 4. A number of ruptured microcapsules are observed, suggesting strong adhesion between the poly(urea-formaldehyde) shell wall and the matrix epoxy resin. The smooth area suggesting fast crack propagation at the impact point is present in all the analyzed samples. By increasing the loading of the spherical additive, the characteristic rough markings disappear gradually as illustrated in Figure 4a-d, suggesting that the presence of microcapsules has an influence on the polymer strength. At 25 wt.% of the additive (Fig. 4e) a rough surface is not present, suggesting the weak and brittle character of the epoxy resin. In this context, the microcapsules are considered as unwanted voids and imperfections (Fig. 5). At higher loading percentages, the microcapsules reduce the polymer area responsible for its strength and resistance to impact.

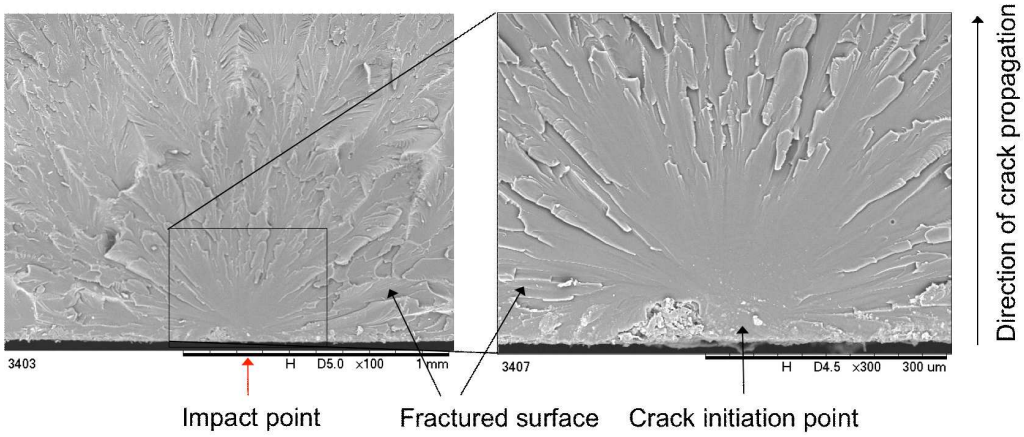

Fig. 3. Fracture surface of neat epoxy resin after Charpy impact test

Rys. 3. Powierzchnia pęknięcia niezmodyfikowanej żywicy epoksydowej po próbie udarności Charpy'ego

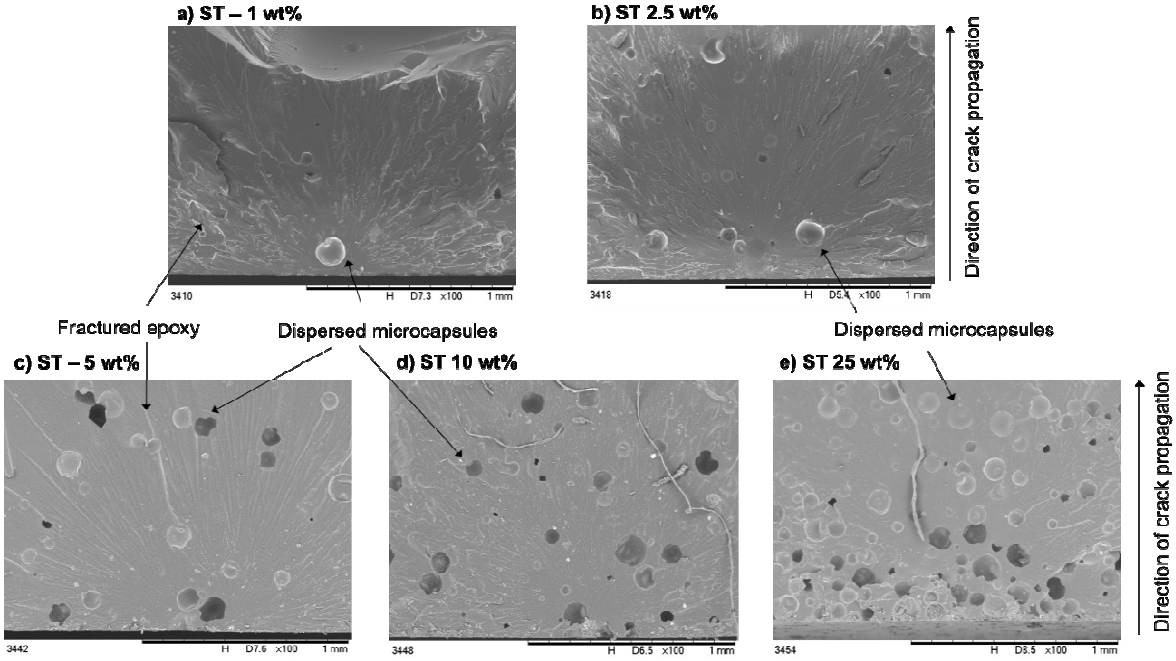

Fig. 4. Fracture surfaces of epoxy resin filled with microcapsules at various loading percentages

Rys. 4. Zdjęcie przełomu kompozytu o osnowie epoksydowej zawierającej mikrokapsułki po teście o różnych frakcjach wagowych mikrokapsułek

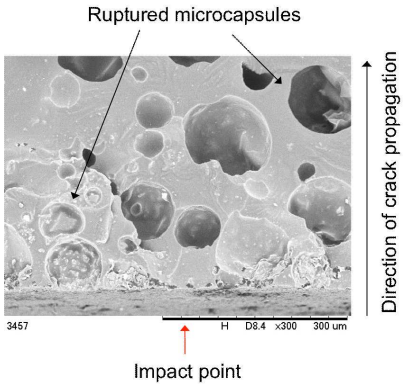

Fig. 5. SEM micrograph illustrating ruptured microcapsules in ST-25 specimen at impact point

Rys. 5. Zdjęcie SEM ilustrujące pęknięte mikrokapsułki w próbce ST-25 w punkcie uderzenia

SUMMARY AND CONCLUSIONS

- Epoxy polymers filled with spherical microcapsules exhibit a significant decrease in strength measured by Charpy impact tests. A maximum 80% reduction was observed for polymers with more than 2.5 wt.% filler and is independent of the microcapsule loading percentage. The samples filled with only 1 wt.% exhibited a 66% decrease when compared to neat epoxy resin. The microcapsules embedded in the polymer exhibit strong bonding with the epoxy resin and easily rupture due to a propagating crack within the material. However, the presence of the spheres in the material is similar to air voids and reduces the fracture cross sectional area and polymer strength.

- The presence of microcapsules affects the surface morphology of the fractured epoxy. At higher loading percentages, no marks suggesting crack arrest were observed. It is characteristic of brittle polymers with low resistance, it is characteristic of brittle polymer with little resistance.
- As the microcapsules have a detrimental effect on ordinary epoxy resin, their fraction in future applications such as self-healing composites should be reduced to a necessary minimum, thus ensuring the minimum effect on the polymer properties and high self-healing performance.

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