EWA ANDRZEJEWSKA[1], MACIEJ ANDRZEJEWSKI[1], JERZY JĘCZALIK[1], TOMASZ STERZYŃSKI[2)*]

Composites of photocured acrylic resins with natural and polymeric fibers

RAPID COMMUNICATION

Summary — The aim of this work was to examine a new family of composites based on the matrix produced of photocrosslinked resins filled with various types of natural or highly oriented synthetic thermoplastics fibers, and finally to examine the properties of such composites in comparison with samples produced from neat photocured resins. The matrix of the composites was the UV-cured epoxyacrylate or epoxymethacrylate resin. The isotactic polypropylene (iPP) fibre, modified with ethylene vinyl acetate (EVA) copolymer, or hemp fibre was used as the reinforcement. An increase in certain mechanical properties was reached in most of the composite materials studied. In case of iPP fibres reinforced composites, a brittle to ductile fracture transition was observed.

Key words: photopolymerization, composites, fibers, mechanical properties.

KOMPOZYTY FOTOUTWARDZALNYCH ŻYWIC AKRYLANOWYCH WZMACNIANE WŁÓKNAMI NATURALNYMI I POLIMEROWYMI

Streszczenie — Celem niniejszej pracy było otrzymanie nowej rodziny kompozytów z matrycą z fotoutwardzalnych żywic akrylanowych, wzmacnianych włóknem naturalnym lub wysokozorientowanym włóknem termoplastycznym oraz zbadanie właściwości tych kompozytów. Matryce kompozytów stanowiły utwardzone promieniowaniem UV żywice epoksyakrylanowe lub epoksymetakrylanowe. Jako wzmocnienie ciągłe zastosowano włókno konopne lub włókno z izotaktycznego polipropylenu (iPP) modyfikowane kopolimerem etylen/octan winylu (EVA). Stwierdzono poprawę pewnych właściwości mechanicznych w większości badanych kompozytów. W przypadku kompozytów wzmocnionych włóknami z iPP zaobserwowano przejście krucho-ciągliwe.

Słowa kluczowe: fotopolimeryzacja, kompozyty, włókna, właciwości mechaniczne.

Polymer composites are widely used for the manufacturing of great variety of products for various applications including modern construction, aeronautical and space technologies. Usually polymer composites are based on thermoplastic or/and thermosetting matrix reinforced with powders, fibers etc. [1—5]. They can be formed during processing of polymers or during the polymerization process [2, 4]. The new idea was to apply the procedure of UV-induced polymerization in order to create the fiber-reinforced composites. Photo-induced polymerization is a rapidly expanding technology [6—13] resulting from its main advantages: the process is far more energy efficient than their thermal counterparts, is economical in the utilization of space, is typically performed in a solvent-less manner that is more environmentally compatible. Moreover, the reaction occurs rapidly at ambient conditions, and the polymerization can be controlled in time.

Low polymerization temperature and high rate of resin hardening makes it possible to produce the composite materials comprising of low heat-resistant reinforcing materials like wood flakes, hemp, cotton, flax etc., but also of highly oriented polymeric high-modulus polyethylene and polypropylene fibers. The most suitable resins for this purpose are multifunctional methacrylate or acrylate oligomers, characterized by a high cure rate, even if a high filler amount is used. As an example the composites used nowadays in dentistry [13, 14] may be mentioned.

Although there are some papers on applications of powder fillers in UV-cured composites [15—19], there are just few information available on the use of fiber fillers in such composite materials. Fernyhough and Fryars [20] patented the use of continuous glass fibers glued with photocurable resin for pulltrusion of reinforced rods. Lackey *at al.* [21] have pointed out the advantages of use of radiation for the curing of composites. The information gained so far in this area was also reviewed in a paper of Endruweit *et al.* [22].

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[1] Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland.

[2] Poznań University of Technology, Institute of Material Technology, ul. Piotrowo 3, 60-965 Poznań, Poland.

[*] Author for corespondence, e-mail: tomasz.sterzynski@put.poznan.pl

The main aim of our work was to examine a new family of composites based on the matrix produced of photo-crosslinked resins filled with various types of natural or highly oriented thermoplastics fibers, and finally to examine the properties of such composites in comparison with the samples produced from neat photocured resins. The obtained products are expected to show improved properties, *e.g.* high impact characterized by ductile type of fracture.

EXPERIMENTAL

Materials

Epoxy methacrylate 97-053 (bis-GMA-bisphenol A diglycidylether methacrylate) (E) and epoxy acrylate resin Genomer 2263 (G), both from Rahn AG (Switzerland) were applied as photocurable resins. Photoinitiator Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1--one from Ciba (Switzerland) was used in concentration 2 wt. %.

The composites were reinforced with two types of fibers:

— the natural hemp fibers (thickness 10 to 50 μm) treated with water, without any special chemical treatment,

— fibers (thickness 20 to 50 μm) produced from isotactic polypropylene (iPP) type Malen (Orlen, Poland), modified with 20 wt. % of ethylene vinyl acetate copolymer (EVA) type Elvax (kindly donated by DuPont).

Sample preparation

The samples of composites and the neat resin samples (in a form of dog bones) for the elongation test were produced in a special steel casting mold. Reinforcing fibers were placed in the matrix in the direction parallel to the main axis of the samples. The samples were irradiated from both sides with middle-pressure mercury lamps.

Methods of testing

The hardness of the samples was measured according to PN-93/C-04206-1 using Shore D apparatus (Stendal, Germany). The mechanical properties by tensile test were determined according to PN-ISO 37:1998 using TiraTest 2000 (Tira, Germany) machine, with a drawing rate of 10 mm/min. From the stress — strain plots the modulus of elasticity (*E*), elongation at maximum stress (ε_{max}) and the elongation at break (ε_b) were calculated.

RESULTS AND DISCUSSION

We have investigated the composites of photocurable resins with natural fibers and fibers made of modified iPP. The use of the latter should offer a special increase in the impact resistance. The compositions of samples and their symbols are listed in Table 1.

Table 1. Compositions (in weight parts) of prepared samples

Symbol of sample	Genomer 2263	Epoxy methacrylate 97-053	Natural hemp fibers	iPP fibres modified with EVA
G	100	—	—	—
G1P	100	—	—	1
G2P	100	—	—	2
G1H	100	—	1	—
G2H	100	—	2	—
E	—	100	—	—
E1P	—	100	—	1
E2P	—	100	—	2
E1H	—	100	1	—
E2H	—	100	2	—

A fairly regular distribution of fibers at the cross section of the samples was achieved. It should be stressed that the aim of introduction of fibers into the photocurable resins was to find whether the effect of reinforcement of the composite may be achieved and/or whether the type of fracture (brittle or ductile) by the tensile test may depend on the type of fibers used in our experiments.

The hardness of the composites is presented in Figure 1. Generally, the addition of fibers causes an increase in Shore hardness of the epoxy methacrylate based composites. In the case of Genomer based composites the addition of EVA modified iPP fibers led to a decrease in hardness, whereas introduction of hemp fibers caused a certain increase in this parameter.

The elongation at maximum force (ε_{max}) determined by tensile test is presented in Figure 2. In both cases, for the epoxy methacrylate based samples as well as for the Genomer based samples, the reduction of ε_{max} value as a result of fiber addition was observed. For the epoxy

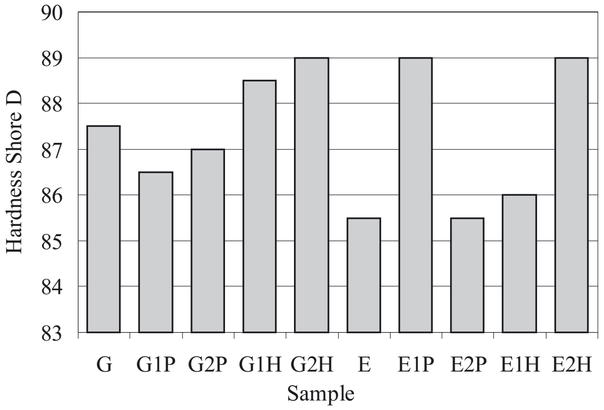

Fig. 1. Shore D hardness of investigated composites; symbol of samples are explained in Table 1

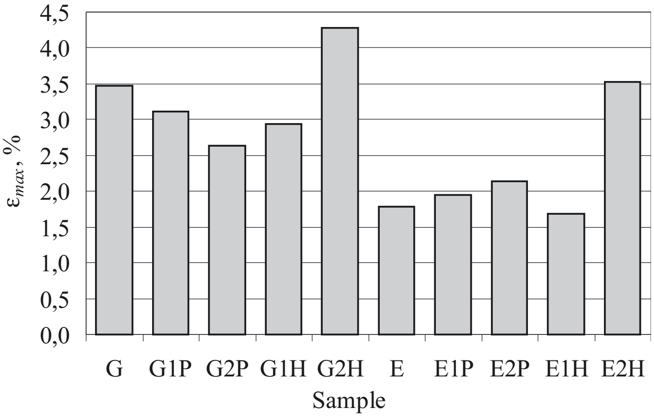

Fig. 2. Relative elongation at maximum stress (ε_{max}); symbol of samples are explained in Table 1

methacrylate samples ε_{max} was about 3.5 %, and the addition of both hemp or iPP fibers led to a decrease in this value to about 1.5—2 %. For the Genomer based composites a decrease of ε_{max} values from about 4.5 % (for the neat resin) to about 2.5—3.5 % (for the composites) was noted. The ε_{max} value corresponds to the stage when a transition from elastic to plastic deformation takes place, or may also signify the strain when the first breaks appear in the elongated sample. Thus, the decrease in ε_{max} value caused by fiber incorporation may be explained by creation of certain resin discontinuity, leading to faster transition from elastic to plastic deformation or/and to lower maximum stress values. As a proof of these observations the changes of maximum stress (σ_{max}) are shown in Figure 3.

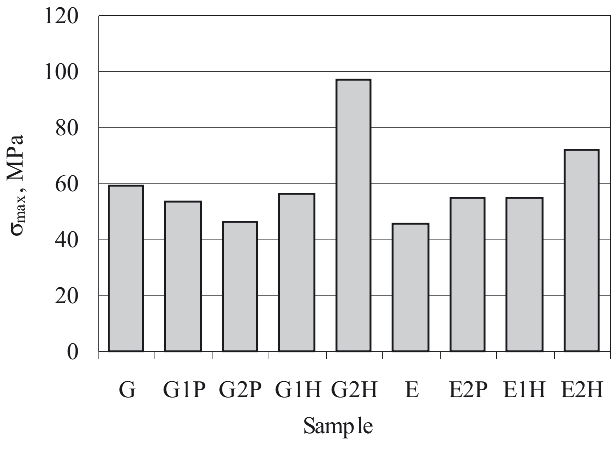

Fig. 3. Maximum stress σ_{max} of the composites samples; symbol of samples are explained in Table 1

As an interesting appearance the changes of *E* modulus values were observed. For the epoxy methacrylate based composites with the addition of iPP or hemp fibers an increase in *E* modulus of about 55 to 70 % was noted. For the neat Genomer samples the *E* modulus equal to 1.31 GPa was found, and only small changes of the elastic modulus were observed (E = 1.39 GPa for composites G1H and G2H) as a result of the addition of hemp fibers. A decrease in *E* modulus was observed for the Genomer based composites with iPP fibers (G1P and G2P).

From the application point of view, not only the stress and modulus values are important, but also the way in which the product behaves at breaking point. Therefore, in certain cases it may be interesting to observe the elongation at break (ε_b), although the fracture by elongation happens after the maximum force was reached, *e.g.* for the deformation domain for which the products usually should not be used.

For the epoxy methacrylate composites the introduction of both, hemp or iPP fibers results in a lower value of ε_b, whereas for Genomer based composites with iPP fibers a positive effect, displayed as a significant increase in ε_b may be noted. This effect is also more visible regarding the samples after reaching breaking point. In the case of neat resin and composites containing hemp fibers the brittle type of break may be seen, signifying a rapid destruction of the product. The composites with iPP fibers are characterized by a ductile type of break, probably due to a sufficiently high adhesion between iPP fibers and the epoxy matrix.

Even if the matrix is totally broken, the product, *e.g.* the dog bone sample in our experiments does not undergo a total distortion. Such behavior may be very advantageous in many applications, in which the product made of photocurable resin is applied in dynamic load condition, and the idea of the construction is to avoid a possible catastrophic distortion of the stress charged parts.

CONCLUSION

The possibility to produce a new family of composite materials based on the photocurable resins with various reinforcing fibers was confirmed. In some cases an increase in certain mechanical properties may be expected. Another interesting result was achieved in the case of iPP fibers reinforced photocurable composites, *e.g.* a brittle to ductile fracture transition. Further investigation with the aim to improve the process ability of such composites is foreseen.

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