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Effect of resin modification on the impact strength of glass-polyester composites

Summary — Fiber-reinforced plastics (FRP) are nowadays used commonly for constructions subjected to impacts of different energies and velocities, therefore the problem of their impact resistance is very important. One of the methods to improve impact properties of the composites is resin modification with elastomeric phase. In this study the effect of resins addition on properties of composites of unsaturated polyester (UP) resins with glass fibers was investigated. At the first stage, the properties of Polimal 109-32K UP resin modified by the addition of reactive liquid rubbers were tested. The wettability of glass fibers by resin compositions was also tested. Composites were then prepared with the addition of 2 and 6 phr of epoxy or vinyl terminated butadiene-acrylonitrile rubbers (ETBN or VTBN, respectively), as well as 5 and 15 wt. % of Polimal 150 elastic UP resin. These composites were subjected to mechanical tests. Impact properties were tested using Charpy method, as well as by a ballistic impact using a gas gun. After the ballistic impact, damage extent and residual strength as well as water leakage through the composites were evaluated. The damage was also investigated under a microscope. The damage extent was confirmed to be linearly dependent on the impact energy. The addition of rubber was found to decrease the damage extent and increase post-impact residual strength, as well as decrease water leakage rate.
Keywords: polymer composites, glass-polyester laminates, resin toughening, reactive liquid rubbers, impact strength, ballistic impact, residual strength.

WPŁYW MODYFIKACJI ŻYWICY NA UDARNOŚĆ KOMPOZYTÓW POLIESTROWO-SZKLANYCH

Streszczenie — Kompozyty poliestrowo-szklane znajdują coraz szersze zastosowania do wytwarzania różnych konstrukcji poddawanych działaniu udarów o różnych energiach i prędkościach. Jednym ze sposobów polepszenia udarności kompozytów może być modyfikacja żywicy poliestrowej, stanowiącej matrycę, dodatkiem fazy elastomerowej. W ramach pracy zbadano wpływ wprowadzenia kauczuków na właściwości kompozytów nienasyconych żywic poliestrowych z włóknem szklanym. Pierwszym etapem prac było zbadanie właściwości poliestrowej żywicy konstrukcyjnej Polimal 109-32K modyfikowanej kauczukami (tabela 2, rys. 4). Metodą elektrooptyczną określono wpływ modyfikacji kompozycji na proces zwilżania włókna szklanego żywicą (rys. 5). Płyty kompozytowe przygotowano z użyciem pętlicowej maty szklanej i żywicy poliestrowej Polimal 109-32K modyfikowanej dodatkiem 2 lub 6 części na sto (phr) kauczuku butadienowo-akrylonitrylowego z epoksydowymi lub winylowymi grupami końcowymi (odpowiednio ETBN lub VTBN) w postaci przedmieszek ze styrenem (50:50). Dla porównania zastosowano również modyfikację żywicą elastyczną Polimal 150 w ilościach 5 i 15 % mas. Kompozyty poddano badaniom mechanicznym, w szczególności udarowym. Właściwości udarowe kompozytów badano metodą Charpy'ego, jak również poddając próbki „ostrzałowi" z użyciem działa gazowego (tabela 1, rys. 3). Po ostrzale, zbadano rozległość powstałych uszkodzeń (rys. 8 i 9), także po udarach wielokrotnych (rys. 10 i 11). Zbadano także wytrzymałość poudarową kompozytów (rys. 12 i 13) oraz wykonano próby przecieku wody (rys. 14 i 15). Przekroje uszkodzeń kompozytów zostały poddane oględzinom mikroskopowym (rys. 16). Potwierdzono liniową zależność powierzchni obszaru uszkodzonego pod wpływem udaru od energii udaru. Dodatek obu stosowanych ciekłych kauczuków reaktywnych zmniejszał rozmiar pola uszkodzeń oraz podwyższał wytrzymałość pozostałą kompozytów, wpływał również na zmniejszenie przecieków wody.

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Słowa kluczowe: kompozyty polimerowe, laminaty poliestrowo-szklane, modyfikacja żywicy, ciekłe kauczuki reaktywne, udarność, udar balistyczny, wytrzymałość poudarowa.

INTRODUCTION

Fiber-reinforced plastics (FRP) are nowadays used commonly for constructions subjected to impacts of different energies and velocities. The constructions comprise, among other: gliders, light airplanes, motorcar and railway vehicle bodies and tank cars, wind turbine blades, roof elements, as well as ballistic protection. The constructions are impacted by hailstones, stones, birds, other constructions and obstacles, as well as firearm projectiles. The problem of impact resistance is very important in these applications.

One of the methods to improve the impact resistance of FRP is a modification of the resin constituting the composites matrix with the addition of elastomeric phase. Modification by the addition of rubber is long used for epoxy resins [1—18]. The reports of such modification of unsaturated polyester (UP) resins are, however, much scarcer [19—30]. It appeared expedient to investigate the influence of rubber addition on properties — especially impact properties, including ballistic impact — of such composites reinforced with glass fiber. The first stage of this work was an investigation of properties of rubber-modified construction-grade UP resin.

Impact events may differ in velocity, energy and mass of impactor, mass of the target and geometry of the setup. Peculiarly important is the velocity of impact — it may be used as a criterion for impact classification after Abrate [31]. The velocity affects, among else, the fracture mechanics of composite matrix material [32].

Low-velocity impacts are the most prevalent and most commonly tested impact events. They are characterized by velocity below 10 m/s. The duration of the impact is much longer than the time needed for an elastic wave to travel to the object edge [31, 33—35]. This type of impact is also labeled as quasi-static due to similar stress distribution [35, 36]. Deciding factor in this instance is support conditions [33, 36]. Such impact is most commonly associated with unintentional collisions and falls from heights. The well known Charpy impact tests fall in this range.

High-velocity impacts, called also ballistic impacts, are characterized by impact velocity in the range of 100—1000 m/s. The duration of the impact is comparable to the time of elastic waves propagation in the direction perpendicular to the surface [31, 35]. Damage is confined to the vicinity of the impact because the elastic waves do not propagate further. The main cause of damage is local excess over material strength on the wave front [31, 33—35, 37]. This type of impacts is most commonly associated with gunfire, shell fragments and collisions of aircraft with various objects.

During an impact event, the impactor dissipates its kinetic energy. In FRP targets, there may occur some or all of the following energy-dissipation mechanisms [33, 37—54]:

— transformation into the kinetic energy of the target moving part,
— fiber deformation,
— fiber failure due to stress exceeding the strength,
— fiber shear,
— delamination and matrix cracking,
— heat release,
— impactor-target friction,
— the deformation of the impactor itself.

In the case of sub-ballistic and ballistic impacts, the greatest share have: kinetic energy of a moving part of the target and fiber destruction [33, 43]. The phenomena such as delamination and matrix cracking, even though their share is relatively meager [33, 43], cause sometimes serious reduction in the residual strength of the material [40, 41, 44, 45, 55—69]. In some circumstances delamination may be the dominant energy dissipation mechanism [33, 46, 51, 61, 70, 71]. Which type of damage dominates depends on impactor parameters and properties of the composite material. The spatial shape of the delamination region has been compared, depending on impact parameters and laminate thickness, to a cone [53, 62, 63], Christmas tree [70], or a barrel [59]. Delaminations after low-energy impact have little effect on the tensile strength, but significantly decrease compression and flexural strength [54, 62, 72, 73]. According to Hirai *et al.* [74] and Imielińska *et al.* [75] no clear correlation between the damage area and post-impact strength is found. Prichard and Hogg [76], however, report exactly such correlation.

The higher the impact energy is, the larger the delaminated region area. The extent of a region delaminated as a result of impact is usually evaluated using one of several nondestructive investigation (NDI) methods: optical image analysis [47, 56, 58, 60, 67, 69, 71, 77—86], air or water-coupled ultrasonic defectoscopy [45, 54—56, 62, 64, 73, 75, 87—103], roentgenography [75, 85, 104—107] and developmental impulsive-thermographic method [64].

An important question is how the impact and impact-induced damage affect the residual strength of a composite panel. Composites residual strength investigation is quite common after low-velocity impacts, but rather uncommon after ballistic impacts. Quasi-static tests of specimens subjected to impact are common. Depending on working conditions envisioned for the material, specimens may be tested for tension [58—59, 67, 93, 99, 108—111], compression [41, 44, 46, 59, 73, 75—77, 86, 88, 89, 93, 98, 100—104], flexion [57, 63, 69, 73, 110, 112] or indentation [110]. Flexural tests are easier to conduct than compressive ones, they do not need special equipment and are not loaded with uncertainties associated to compressive tests [72]. Besides quasi-static post-impact tests, follow-on impact tests are also conducted [56—58, 60, 67, 107]. Post-impact tests may also include fatigue tests [108].

The objective of this work was to investigate the effect of different toughening agents [elastic unsaturated polyester (UP) resin and two kinds of reactive liquid rubbers — epoxy or vinyl terminated butadiene-acrylonitrile copolymers (ETBN and VTBN)] addition in glass/polyester composites on the extent and characteristics of the field of damage resulting from high-velocity impact of known energy, as well as on the residual strength of the damaged composite material. Resin compositions were tested both as liquids (some of the results published in [113]) and as cured castings (results of standard mechanical tests published in [114, 115]). Obtained results were utilized for selection of compositions, which were subsequently used to produce composites for the investigation (preliminary results of standard mechanical tests published in [116]). Summary of previously published results will follow. The viscosity of compositions with both rubbers was higher than basic resin and its compositions modified with elastic resin [113]. Additions of modifiers led to lengthened curing time of the compositions and usually lowered the temperature maximum of the reaction. It is especially visible in the sample with addition of 15 wt. % of elastic resin and in the sample with 10 phr of VTBN rubber [113].

Mean results of examined mechanical properties of resin castings do not exhibit, in the general sense, any clear and established tendencies of change dependent on the type and amount of introduced modifier. All modifiers increase elongation at break, decrease hardness, and decrease Young's modulus. The rubber modifiers lead to decreased flexural modulus [114, 115].

An interpretation of the results of standard mechanical tests is problematic. The addition of modifiers affected different properties in different ways. Addition of elastic resin decreased both elastic moduli. Application of both rubbers tended to increase the moduli and strengths. The greatest increase (reaching 25 %) in strength is noted for laminates with resin modified with the addition of 2 phr of both examined rubbers. The modifiers do not induce significant decrease in interlaminar shear strength, and the addition of ETBN even increases it considerably [116].

EXPERIMENTAL

Materials

The composites used in this work were manufactured from construction-grade unsaturated polyester (UP) resin under the name Polimal 109-32K produced by Z.Ch. „Organika-Sarzyna" (Poland).

This resin was modified using two kinds of reactive liquid rubbers produced by Emerald Performance Materials (USA): epoxy-terminated butadiene-acrylonitrile copolymer Hypro ETBN 1300 x 40 (dubbed ETBN from now on) and vinyl-terminated butadiene-acrylonitrile copolymer Hypro VTBNX 1300 x 33 (dubbed VTBN from now on). The ETBN rubber was supplied as a solution in styrene (in proportion 1:1). For comparison, elastic UP resin under the name Polimal 150 (production Z.Ch. „Organika-Sarzyna", Poland) was used.

The resin compositions were cured using a system consisting of 0.6 cm^3/kg of 10 % cobalt accelerator (made by ILT, Poland) and 1.5 phr of methylethylketone peroxide (MEKP) initiator under the name Metox 50R (made by Oxytop Sp. z o.o., Poland).

As a composites' reinforcement, a glass-fiber continuous-filament mat was used. The mat was Vetrotex Unifilo U750 450-138 with areal weight of 450 g/m^2 with silane surface treatment and thermoplastic-polyester binder. The elementary fibers were determined to have a diameter in the range of 16—21 μm.

Sample preparation

Resin-modifier composition

Modified compositions were made using rubber premixes in styrene (1:1). Presented numbers represent the amount of such premix. The modifiers were added to the basic resin in the following amounts:

— 5, 10 or 15 wt. % of Polimal 150 (samples labeled as 5P150, 10P150, 15P150, respectively);

— 2, 6 or 10 phr of ETBN rubber (samples labeled as 2ETBN, 6ETBN, 10ETBN, respectively);

— 2, 6 or 10 phr of VTBN rubber (samples labeled as 2VTBN, 6VTBN, 10VTBN, respectively).

The unmodified basic resin was labeled P109.

Composites

The composite plates were prepared using the continuous filament mat and the UP resin Polimal 109-32K modified with additions of 2 or 6 phr VTBN and ETBN premix (with styrene, 1:1). The 5 or 15 wt. % additions of Polimal 150 elastic resin were used for comparison.

The composite plates for testing, size 520 × 520 mm and 4 mm thick, were prepared by the resin transfer molding (RTM) technology. GEPO type RTM mini aggregate was used. 1.5 phr of MEKP was added as an initiator, and 0.6 cm^3/kg of 10 % cobalt accelerator was used. The infusion of six plies of reinforcing mat by the resin was conducted through central inlet, and the air and excess of resin was removed through four outlets in corners of the stiff two-part mold. Resin curing was conducted at the room temperature.

The volume fraction of glass fiber in formed composites is 23 vol. %, and the mass fraction is 39 wt. %. Poro-

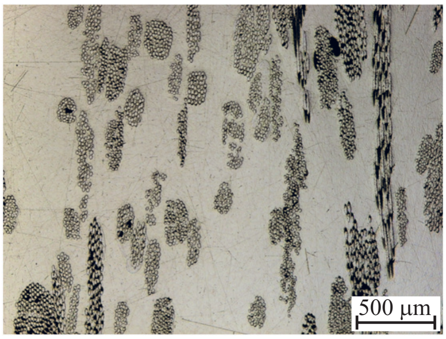

Fig. 1. Microsections of continuous-filament mat-reinforced composite of P109 with 23 % fiber volume fraction (magnification 100×, porosity 2.9 vol. %)

sity of the composites amounted to 1.8—3.5 vol. %. Microstructures of the composites are exemplified by the microsection in Figure 1.

Methods of testing

The progress of the curing reaction of the compositions was investigated by temperature plot as it was described in [113] and by differential scanning calorimetry (DSC). The latter was conducted using Q100 differential calorimeter (TA Instruments). Each composition was mixed with the accelerator. Immediately before the test, a composition was mixed with the initiator and then a sample of about 15 mg of the composition was put into the calorimeter. The sample was then heated at constant rate of 10 K/min from 0 to 200 °C. Exothermic heat of the curing reaction was measured as an area of the peak between the curve and the baseline.

Sections of cured cast samples were subjected to microscopic examination using Carl-Zeiss-Jena Jenavert optical microscope equipped with Panasonic color CCTV camera model WV-CD132L for image capture. This microscope allowed examination of samples with magnification from 64× to maximum 1000×. Introduced rubber modifiers in hardened castings of the composition constituted separate phase, dispersion of which was dependent on rubber type and amount.

An important parameter of composite-manufacture technology is the wettability of reinforcement by the resin. No or bad wetting increases the porosity of the composites structure, hinders adhesion development between the reinforcement and matrix, and impairs properties of composites. The wettability of Unifilo mat by the resin compositions were tested with the electro-optical method, which is presented in Figure 2. There is measured the change in the current induced in the sensor circuit as the wetting proceeds. The dispersion of light transmitted through the wetted sample decreases with the progress of wetting, and stabilizes when the wetting is complete.

Impact properties of the composites were tested with two different techniques. The first one was Charpy impact testing with instrumented hammer having the impact energy of 5 J and strike velocity of 2.9 m/s. This test was conducted according to ISO 179-2:1997 standard.

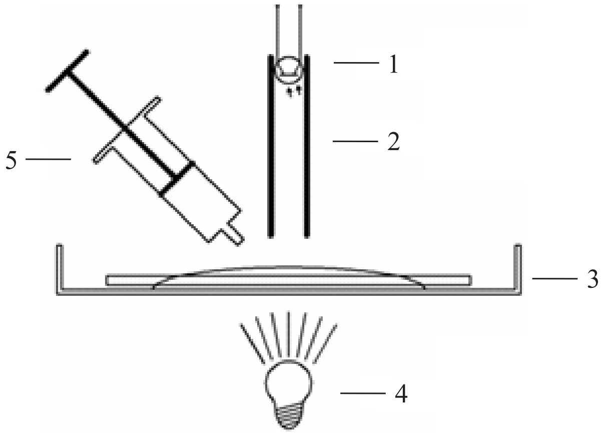

Fig. 2. Scheme of the system for wettability measurements: 1 — photodiode, 2 — collimator, 3 — Petri dish with single ply of reinforcement, 4 — light source, 5 — syringe with resin (composition)

The second test encompassed subjecting 100 × 100 mm plates freely supported in the corners to central impacts by a steel ball of 8 mm diameter and mass of 2 g. The impactor muzzle velocity is measured by an attached ballistic chronograph. The difference between the muzzle and incident velocity is deemed negligible due to the short distance between the barrel muzzle and the sample. The impactor velocity was changed by varying the compressed air pressure. Such „gunfire" on the composites was conducted at four different velocities and energies, as laid out in Table 1. This means the impacts fell in sub-ballistic and ballistic regimes. There is a distinct dearth of publications for such tests of glass-polyester composites. This test was conducted using specially built pneumatic test assembly shown in Figure 3.

T a b l e 1. Velocity and energy of the impactor (ball)

Impactor velocity, m/s	Impactor energy, J
88.1 ± 0.6	7.76 ± 0.11
101.1 ± 1.0	10.22 ± 0.20
113.7 ± 1.4	12.94 ± 0.33
126.9 ± 1.0	16.11 ± 0.26

The ballistic damage to the plates was evaluated with the following methods:

— measurement of the damage area as visible in transmitted light,

— post-impact mechanical tests of the damaged plate and calculation of the residual strength of the damage region alone,

— evaluation of the damage escalation after subsequent impacts into the damaged plate,

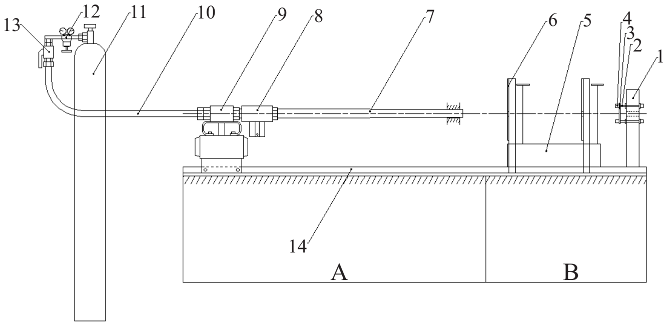

Fig. 3. Scheme of the ballistic assembly: A — propelling part, B — measurement part, 1 — base plate, 2 — specimen support, 3 — specimen, 4 — magnet, 5 — ballistic chronograph, 6 — anti-blast screen, 7 — barrel, 8 — receiver, 9 — electro-pneumatic valve, 10 — compressed-air duct, 11 — compressed-air tank, 12 — gas reductor, 13 — shut-off valve, 14 — montage rail

— assessment of the leakage of water through the damaged plate under given water column,

— microscopic examination of the damage in microsections of the plates.

The extent of delamination (co-occurring with matrix cracking) was evaluated by means of digital image analysis — the samples were photographed in transmitted light using a digital camera. The obtained images were processed using Scion Image software to measure the contrasting delaminated area.

In order to evaluate the residual load-bearing abilities of the composites, the samples were tested under quasi-static three-point bending conditions, both after the ballistic impact and without prior impact. Three-point quasi-static bending was conducted on an Instron 4206 universal testing machine with computerized data acquisition. The samples were square plates 100 × 100 × 4 mm. Due to their nonstandard width, the testing method was based on the ISO 178:1996 standard (Plastics — Determination of flexural properties), but modified to suit the specific experimental needs. The literature advises presenting the post-impact strength for the entire impacted plate. In this work, besides thus presented post-impact strength, residual strength of the damaged region alone was calculated according to a method elucidated in previous publications [118, 119].

A multiple impact test was also performed, in which a sample was repeatedly impacted at the point of the original impact, with constant energy equal to 16 J, as many times as was required to achieve complete perforation of the target sample.

Water leakage was tested by placing the damaged sample under 500 mm column of water. The volume of water leaking through the material in a given time was measured.

Selected samples of each material damaged by the impact were sectioned using diamond saw diagonally through the field of damage. The resulting surface was then prepared through grinding and polishing and investigated using a 3D scanning laser microscope Keyence VK-9700 series. For each sample, several images were made, encompassing the whole area of the section. The individual images were than assembled into one large image.

RESULTS AND DISCUSSION

Properties of the resin compositions

The results of DSC-obtained heat of reaction, as well as results of previous rheology and curing tests [113] are presented in Table 2. The heat of reaction of all compositions is lower than for the basic resin. The higher addition of modifier, the lower the heat of reaction is.

T a b l e 2. Heat of reaction for all compositions obtained using DSC and results of previous investigations (viscosity, peak temperature during curing and time to the peak temperature from the temperature plot)

Symbol of composition	Heat of reaction J/g	Viscosity [113] m·Pas	Peak temperature [113], °C	Time to the peak temperature [113], min
P109	357.5	475	131.2	27,75
5P150	292.8	480	124.6	34,75
10P150	277.1	535	118.4	41,75
15P150	243.6	585	112.5	50,00
2VTBN	334.4	545	136.5	36,50
6VTBN	330.7	750	122.8	48,75
10VTBN	276.8	910	104.1	61,00
2ETBN	285.1	535	119.6	33,83
6ETBN	262.3	775	111.6	35,08
10ETBN	275.7	1070	127.2	39,67

Micrographs presented in Figure 4 illustrate exemplary morphologic structure of compositions with both rubbers. The precipitations of elastomeric phase proved to be heterogeneous. In their interior, especially the larger ones, secondary precipitations are found. Precipitated particle sizes in compositions with VTBN were visibly larger than in compositions with ETBN. The diameters of particles in compositions with VTBN were in the range of 30—100 μm, while in compositions with ETBN only 10—30 μm. More in-depth analysis of the rubber-modified resin morphology, as well as characterization of the precipitated phase, will constitute separate publication.

Figure 5 presents the progress of wetting by basic resin and modified compositions. The wetting behavior of modified resins does not vary considerably from the wetting behavior of the basic resin. The modifiers do not worsen this significant technological parameter of composite production.

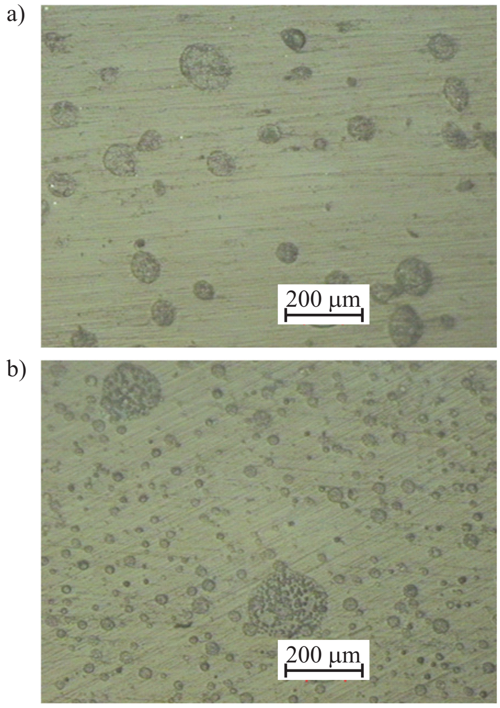

Fig. 4. Microsections of cured castings (magnification 320×): a) 10VTBN, b) 10ETBN

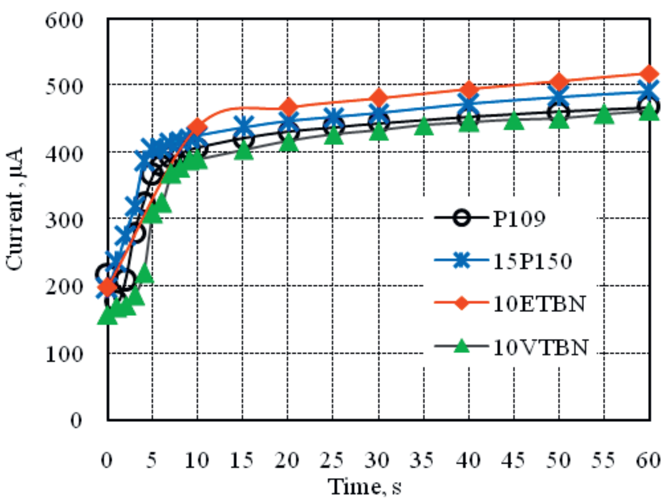

Fig. 5. Graph of the current induced in the sensor circuit versus time for different compositions during wetting of continuous-filament mat

Impact properties of the composites

Results of Charpy impact tests

Examples of curves obtained in instrumented Charpy impact tests, as a force-time function, are illustrated in Figure 6. The curves have the same general shape for all of the composites, but numerical differences exist. Mean peak force and the impact strength for each composite are shown in Figure 7.

Breaking of specimens occurred at approximately 2.0—2.5 ms after the impact and at 6—7 mm deflection.

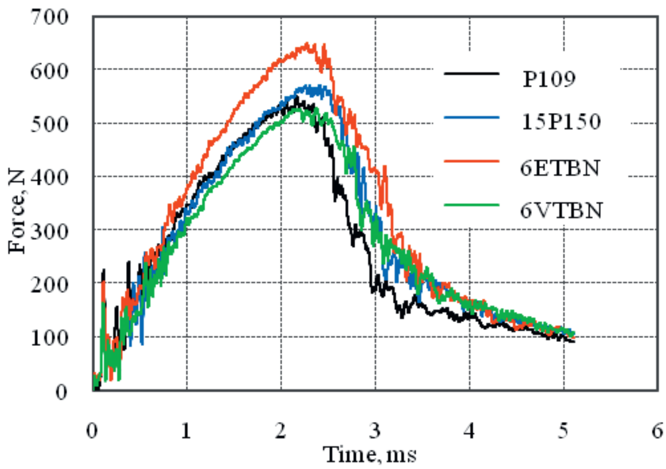

Fig. 6. Force versus time during Charpy impact tests averaged for composites with selected resins

Polyester matrix modifications did not significantly influence either the force history or its peak value, two instances excepted. Composite with 5 wt. % addition of elastic resin exhibited considerably lower (approx. 500 N) than normal (approx. 600 N) peak force value. The composite with the matrix modified by 6 phr of ETBN rubber addition exhibited considerably higher peak force value (approx. 700 N). These differences are visible in the force history.

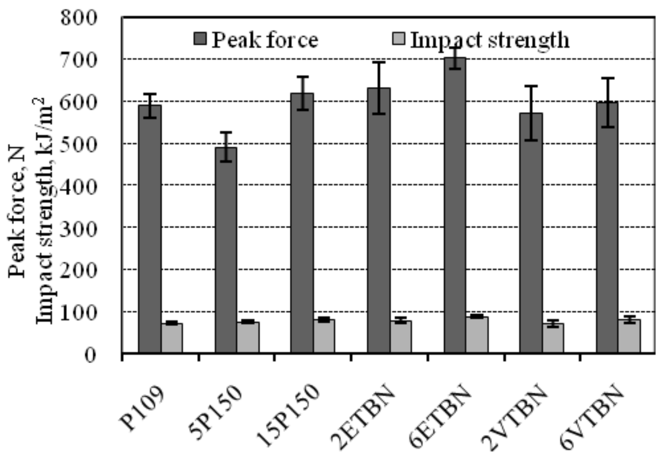

Fig. 7. Mean peak force and impact strength in Charpy impact tests of the composites at 0.95 confidence level

Mean Charpy impact strengths of the composites calculated from the force history demonstrate, that even small addition of a modifier significantly improves toughness of the composite and thus its impact strength. The greatest effect had an addition of ETBN rubber. Even 2 phr addition of the rubber leads to similar effect as 15 wt. % of Polimal 150 elastic resin. 6 phr addition increases the impact strength of the composite by 25 % compared to unmodified composite. The improvement correlated with ETBN rubber addition defies some previous publications [20, 30] stating reactive liquid rubbers have no such effect on impact strength of glass-polyester laminates.

Ballistic tests

Examples of transmitted-light photographs of the back side of specimens subjected to ballistic impact are illustrated in Figure 8. The damage area dependence on the impact energy, presented in Figure 9, was linear for all of the composites and the correlation coefficient was found to be significant, in the range 0.8776—0.9788.

There is no visible difference between composite with basic resin and composites with matrix modified by the addition of Polimal 150 elastic resin. Within composites modified by the addition of rubber, the small difference is present. The greater the addition of rubber, the smaller the area of damage. This effect is more significant in VTBN-modified composite than in ETBN-modified one.

a)

b)

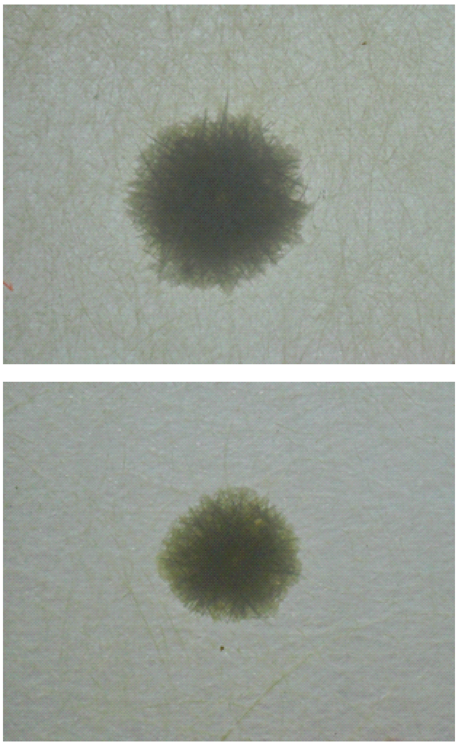

Fig. 8. Transmitted-light photographs of the back side of specimens of the composite with basic resin after ballistic impact: a) after 16 J impact, b) after 7 J impact

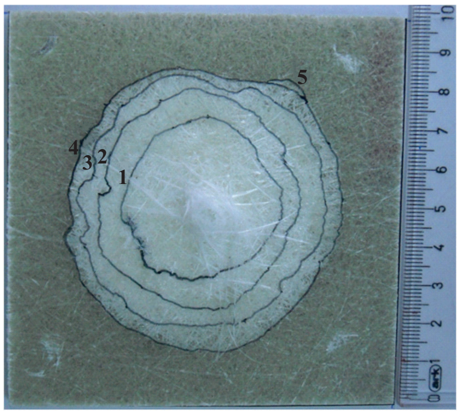

Fig. 10. Photograph of a plate of basic-resin composite after 5 consecutive 16 J impacts (contour of the damage extent after each impact is delineated with a marker)

Interesting information about impact properties is given by repeated impact tests. Such tests were conducted on a small number of specimens due to shortage of material. After consecutive impacts, the extent of damage region increases, which may be illustrated by a photograph in Figure 10. Subsequent Figure 11 illustrates the extent of the damage area after consecutive impact

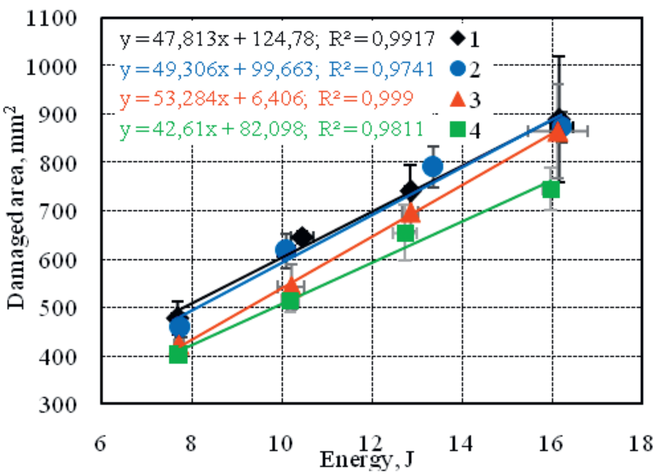

Fig. 9. Mean damage area of the composites versus ballistic impact energy for: 1 — composite without modification, 2 — composite with 15P150, 3 — composite with 6ETBN, 4 — composite with 6VTBN

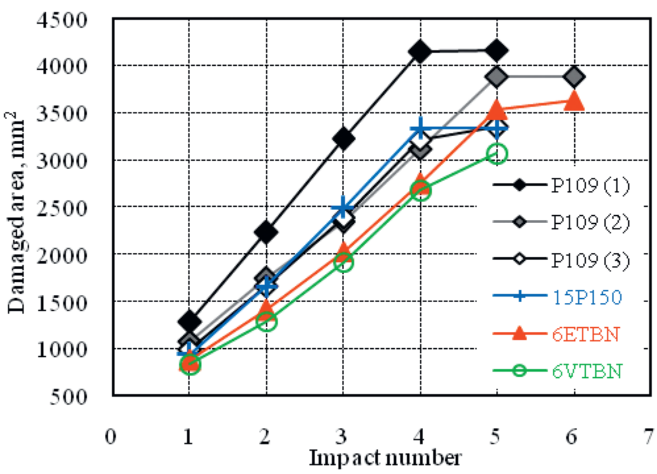

Fig. 11. Damage area after consecutive impacts (16 J of energy) in repeated-impact test (numbers in parentheses indicate consecutive specimens of the same material)

into the composite with standard and modified matrix. The last point of each of the lines corresponds with perforation of the plate. The growth of the damage area is directly proportional to the number of impacts. The growth was slightly slower in both of the composites with rubber-modified matrix. Perforation was achieved at the 5th or 6th impact.

Post-impact residual strength

Especially interesting results of residual strength of the damaged region for composites with different matrix modifications are illustrated in Figure 12. The influence of the matrix is clearly visible here. Composites with modified matrices exhibit higher residual strength than the composite with unmodified matrix. The higher the addition of modifier, the higher residual strength of the damaged region was. In the case of matrices with high addition of modifiers, the residual strength reached even approx. 100 % — that is the strength of the undamaged material. This was somewhat of a surprise. Lower bounds of the confidence interval amount in this case to approx. 80 % of the value for undamaged material. Interpretation of this result is indeed problematic. It is reflected, however, in the results of repeated impacts presented above: the damaged region was not perforated even after four consecutive impacts, which proves that it was still able to successfully bear the loads.

Also, some correlation between the residual strength of the damaged region and Charpy impact strength of the material was found and it is presented in Figure 13. Standardized Charpy impact test gives, therefore, some information on the residual strength of composites.

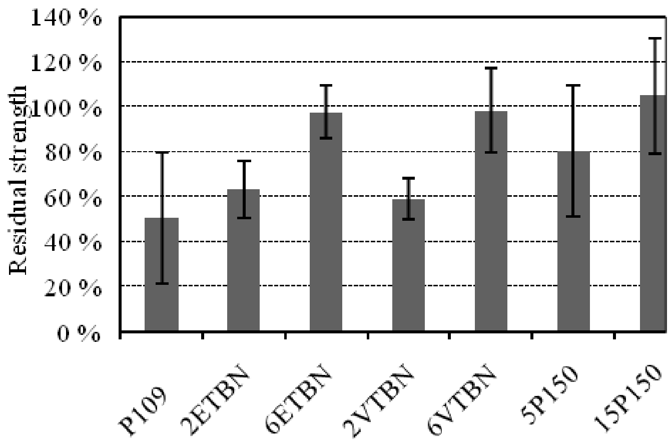

Fig. 12. Averaged percentage of residual flexural strength of the damage regions of composites with various matrices after impact of mean energy 11.5 J

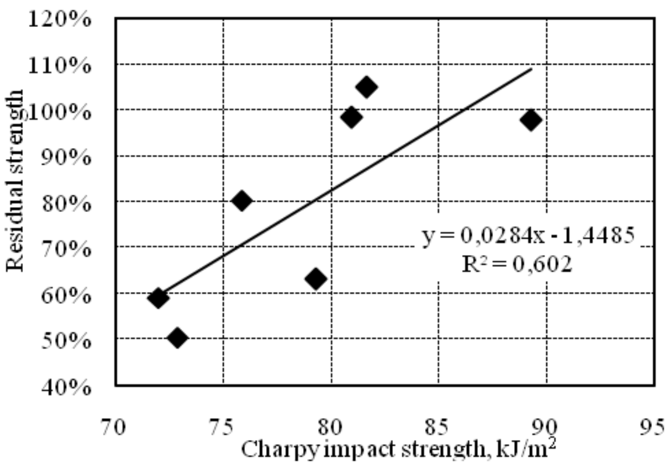

Fig. 13. Correlation between the percentage of residual strength of the damaged region for composites with various matrices and Charpy impact strength

Water leakage test

An interesting evaluation of the damage severity is given by testing water leakage through the impact-damaged composite plate [120, 121]. Composites after single impact did not exhibit notable leakage in a short time. As it is presented in Figure 14, significant leakage in a short time appears only after multiple impacts. Consecutive impacts lead to much faster leaking. The damage after consecutive non-penetrating impacts is not only greater in the extent (Fig. 11) but also in severity, including an open web of fissures.

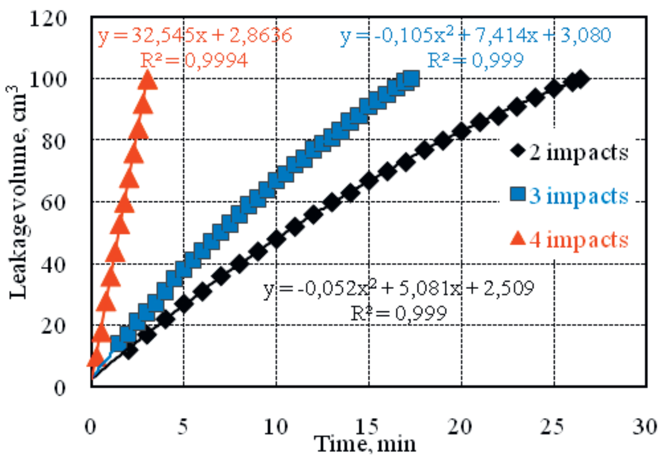

Fig. 14. Leakage volume versus time for composite with mat and basic resin after 2, 3 and 4 consecutive 16 J impacts

The influence of matrix modification on the rapidity of water leakage in long time is illustrated in Figure 15. After high-energy impacts (16 J), the rate of leakage is high and it is similar in composite with basic matrix as well as with modified matrices — approx. 0.7—0.8 cm^3/h. The composite with 6VTBN matrix exhibited, however, only half of the rate exhibited by unmodified composites. After lower-energy impacts (10 or 13 J), the influence of modifiers was considerably smaller: the lower the impact energy, the lower the effect of modifier reducing the leak-

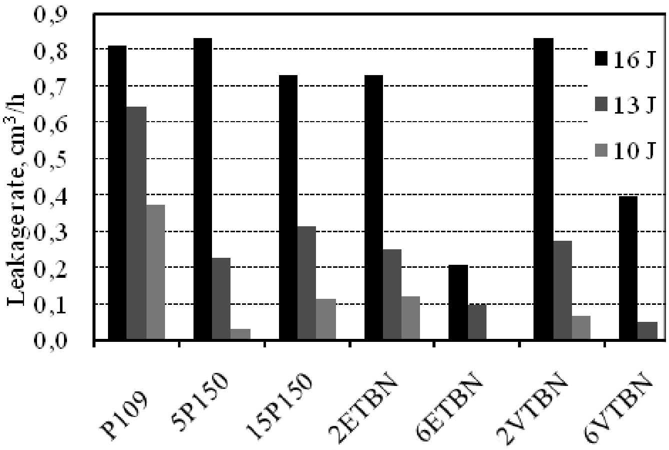

Fig. 15. Mean leakage rate through different composites in a long time (24 h)

age rate. After 10 J impact, there was no measurable leakage in the composite with 6VTBN matrix. These properties may have significance in the case of application of composites for production of marine devices as well as various tanks for liquids.

Morphology of composite sections after impact

The morphology of sections of impacted composite plates with all matrices reinforced with continuous filament mats was similar. The example of such morphology is presented in Figure 16.

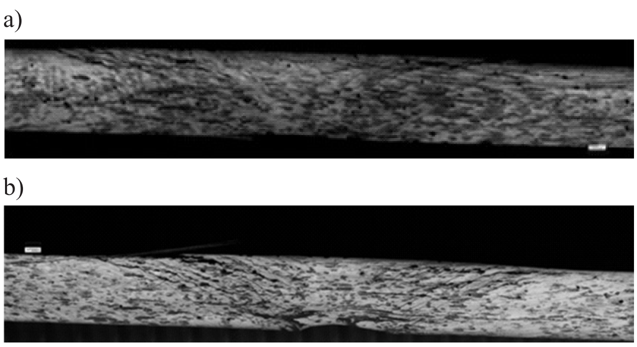

Fig. 16. Microsection of composite with basic resin after 7 J (a) and 16 J (b) impact

In the microsections one can observe oblique microfractures delineating side-surface of a cone, the interior of which is virtually undamaged. The oblique fractures are the cause of the water leakage. After low energy impacts, as well as in composites with large addition of modifier, the fractures are lower in number and less apparent. In the point of impact more- or less-pronounced crater is present. A part of the composite directly beneath the point of impact acts during the impact relatively to the rest of the material as a conical plug. On the border of this region, shearing stress occurs, which leads to the appearance of the oblique fractures. Tests with woven-roving reinforcement, which were also conducted, exhibited delaminational fractures and, therefore, no water leakage. Micromechanism of the damage development depends on the type of matrix, type of reinforcement, as well as on impact energy.

CONCLUSIONS

— Both kinds of reactive liquid rubbers (ETBN and VTBN) precipitate on curing. The dispersal of such precipitates depends on the kind and amount of the rubber. The precipitated particles are heterogeneous in structure.

— Modifiers induce different changes to mechanical properties of cast compositions without significant tendencies.

— Reactive liquid rubbers and the elastic resin (Polimal 150) lead to approximately two-fold increase in viscosity and curing time. No impairment of wetting of the reinforcing glass fibers was observed, however.

— The addition of reactive liquid rubbers and the elastic resin did not impair forming the composite with the RTM technique.

— Linear dependence of the damage area on the impact energy was confirmed in all tested composites with different modifications of the UP matrix. Obtained coefficients of correlation are close to one.

— The addition of both of the reactive liquid rubbers used decreases the damaged area and increases residual strength of the composites. The cross-sections of the induced fractures are observed to decrease as well, as illustrated by the water leakage test. Even small addition of a modifier may significantly improve fracture toughness, as well as the impact strength of the material. The increase in the case of rubber modification occurs without significant impairment of the rest of tested mechanical properties, especially flexural strength and modulus. The increase observed in ETBN-modified composites disagrees with some reports [20, 30].

— Post-impact strength of the damaged region accounts for from 50 up to approx. 100 % of the flexural strength of an undamaged composite. The damaged region was also resistant to consecutive impacts (perforation occurred only after 5—6 impacts).

— Some correlation between standardized Charpy impact test and the residual strength of the ballistic-impact damaged region was found.

— Obtained data permit the choice of best modifications of the polyester matrix in the direction of impact resistance without significant diminishing of other mechanical properties. Composite with addition of 3 phr VTBN rubber may be adopted as the best modification. Thus modified composites exhibit the smallest damage area and one of the highest impact strengths. Properties of composites with addition of ETBN rubber are close to those with VTBN — the effect on the damaged area is smaller, but such-modified composites exhibit slightly higher Charpy impact strength and static properties. Elastic resin modifications, however, did not decrease the damaged area, slightly increased the impact strength and lead to decrease in mechanical properties.

ACKNOWLEDGMENTS

This work was financed by the Ministry of Science and Higher Education of the Republic of Poland in project N507 290339.

Authors would like to thank Nanoresins AG company for supplying the reactive liquid rubbers used in this study.

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Received 4 VII 2012.

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