

Preparing, properties and application of waterborne polyurethane-acrylate oligomer as a matrix in UV-cured fiberglasses

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Submitted October 18, 2016 ; Accepted February 12, 2017

Waterborne polyurethane-acrylate oligomer-(WPUA) was prepared via in-situ and anionic self-emulsifying method from Hexamethylene diisocyanate (HDI), polyether polyol (Lupranol 1000/1), dimethylolbutanoic acid (DMBA), and capped with 2-Hydroxyethyl methacrylate (2-HEMA). Then Ultraviolet (UV) curable fibreglass prepreg was obtained from WPUA oligomer, 2-hydroxyethyl acrylate (2-HEA) as reactive diluent, Irgacure 500 as photoinitiator and glass fabric of different weight (81; 163; 660g/m²). The physical properties of produced WPUA oligomers, such as IR spectra (by Fourier transform infrared spectroscopy), particle size distribution and apparent viscosity were investigated. Mechanical properties of UV-cured fibreglass composites, such as tensile strength, elongation at break and thermal properties DSC (Differential scanning calorimetry), of UV-cured composites were determined. The specific UV-WPUA was selected as a material with many applications. The results indicate that the prepared UV-WPUA is suitable as matrix material for UV-curable fibreglass composites.

Keywords: waterborne polyurethane-oligomer, UV-curable fiberglasses, mechanical and thermal properties

INTRODUCTION

Polyurethanes (PUs) are used in a surprising array of commercial applications [1]. They are also unique polymeric materials with a wide range of physical and chemical properties [2]. Polyurethanes are usually used as adhesives, coatings, foams, and different kinds of plastics and elastomers, as well as matrix for polymeric composites [3]. Recently, waterborne polyurethane (WPU) has been developed largely because of its excellent mechanical properties, fire resistance, low toxicity and lack of environmental hazards [4]. The waterborne polyurethanes using ultraviolet (UV)-curing technology have gained increasing interests due to their advantages such as low energy consumption, high chemical stability, cost efficient and high curing speed [5]. Light-induced polymerization of multifunctional monomers or oligomers, also called UV-radiation curing, has become a well-accepted technology which has found a large variety of industrial applications because of its unique advantages [6]. UV-radiation curing has been successfully used to produce polymer composites [7]. This is the process of film transformation from a reactive liquid (except a powder) into a solid by radiation in the ultraviolet-energy region rather than by heat. UV cure coatings involve the polymerization and crosslinked polymer network induced by photons and are one of the most

important classes of coatings [8]. The most extensively used UV-curable resins are based on acrylate, which exhibit high reactivity, i.e. short reaction times in the order of magnitude of fractions of a second, and offer a large choice of monomers and telechelic oligomers with functional end groups. Acrylate-based resin systems typically consist of three basic components namely, acrylate functionalised oligomer, which forms the backbone of the polymer network, acrylate monomers (small molecules containing one or more vinyl groups) and photoinitiator, which generates free radicals on UV exposure [9]. Furthermore the high reactivity of acrylates leads to a fast photopolymerization process and saves time in industrial processes [10]. Also in the UV-curing technology of waterborne polyurethanes is usually used acrylates as a reactive diluents. They are some of these ingredients which dilute the oligomer to reduce its viscosity in order to conveniently coat on a suitable substrate prior to making the polymer film, and the second function is the participation of the diluent in the reactive process of the oligomer with a view of making a polymer with a desired property for some specific purpose [11]. In the present study, WPUA was synthesized with polyether polyol, 2,2-dimethylolbutanoic acid 2-hydroxyethyl methacrylate and hexamethylene diisocyanate. WPUA synthesis was carried out in flowing nitrogen atmosphere. These aqueous polyurethane dispersions and their dried polymer

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films were characterized and confirmed for the formation of urethane linkage. Laminated products are prepared from layers of materials bonded together forming a unit body. Laminated plastics are produced in large volumes by the industry in the form of laminated sheets, tubes, rods and a multitude of products employing such materials as paper, asbestos, cloth, wood cellulose, glass fabric (fiberglass), etc., bonded together by synthetic resins [12]. In these case UV-curing waterbased polyurethane is a matrix for bidirectional fiberglass reinforced composites.

EXPERIMENTAL

The materials, which were used in this experiment are:

- Polyether polyol (Lupranol 1000/1, $M_n = 2000$ g/mol) was produced by BASF Polyurethanes GmbH, Lemförde, Germany
- 2,2- dimethylolbutanoic acid (DMBA)
- 2- Hydroxyethyl methacrylate (2-HEMA)
- 2-Hydroxyethyl acrylate (2-HEA)
- Triethylamine (TEA) were supplied from Sigma Aldrich Chemie GmbH
- Desmodur N3300 - Aliphatic polyisocyanate (HDI trimer) was produced by Bayer MaterialScience AG, Leverkusen, Germany
- Dibutylbis (lauroyloxy) tin (DBTL) PC CAT T12 was produced by Performance Chemicals Handels GmbH Irgacure 500 were supplied from BASF Schweiz AG, Germany.

Preparation of UV- PUA oligomer

A certain amounts of Lupranol 1000/1 (10.802 g) and HDI (8.325 g) were added into a four-necked flask equipped with a mechanical stirrer, thermometer and reflux condenser. Then, PC CAT T12 was added as catalyst and the mixture was heated to 45-55°C and keeping the temperature for 1 h. to prepare the -NCO terminated prepolymer. Next, the above prepolymer was reacted with a certain amount of DMBA (1.221 g) dissolved in small amount of acetone at 45-55°C for another 2 h, and the -NCO terminated prepolymer containing carboxyl group was obtained. 2-HEMA (4.875 g) was added into the system and reacted at 45-55°C for 3-5 h. When the temperature was cooled down to 40°C, TEA were added into the flask subsequently and reacted at 40°C for 30 min. The mixture was then dispersed into deionized water at 30°C under vigorous stirring for 30 min. The synthetic route of WPUA oligomer is shown in Figure 1.

Particle size distribution of the oligomers

For the determination of the particle size distribution of WPUA oligomers WPUA sample materials were filled to 5-ml test tubes and diluted with deionized water. The particle size was determined by light scattering with the laser particle size analyzer (Zetasizer Nano S Malvern Instruments Limited) according to ISO 13320:2009.

The apparent viscosity of WPUA oligomers

The apparent viscosity of the WPUA oligomer was measured by a rotational viscometer (Anton Paar Physica MCR 301) according to ISO 3219:1993 Plastics-Polymers/resins in the liquid state or as emulsions or dispersions. Determination of viscosity using a rotational viscometer with defined shear rate; when the shear rate was 2000 s^{-1} , the high shear rate warranted highly reliable measurements at a temperature 25°C.

IR spectra of the matrix

FT-IR spectrum of the matrix was obtained according to ASTM E1252 - Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis between 4000 and 400 cm^{-1} with an FT-IR spectrometer (Varian 620- IR, FT-IR). A minimum of 16 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4000 – 400 cm^{-1} ranges.

Preparation of UV- curing fiberglass composites

WPUA fiberglass composites were prepared by casting the newly synthesized oligomer and glass fabric of different weight (81; 163; 660g/m²) onto a teflon plate drying at 65°C for 3 h. Because water was used as diluents in this system, a flash-off step is needed, to remove the water by evaporation before UV-curing. During the water removal from the aqueous dispersion, physical entanglement occurred because of the large molecular weight of the prepolymer. Then was irradiated with the UV light from a lamp (main wave length: 365 nm, the power of the lamp: 400 W, Spectral UV-A emission 1200 mW/m² and distance between the thin film samples and the center of UV lamp of 15 cm). The Irgacure 500 was activated and radicals for the polymerization could be produced. The formed radicals react at the acrylate double bond of the monomers and oligomers forming polymers under crosslinking and the WPUA fiberglass composite is obtained. The waterborne WPUA matrix was cured through a two-step process. The photo-dissociation mechanism of Irgacure 500 is shown in Figure 2.

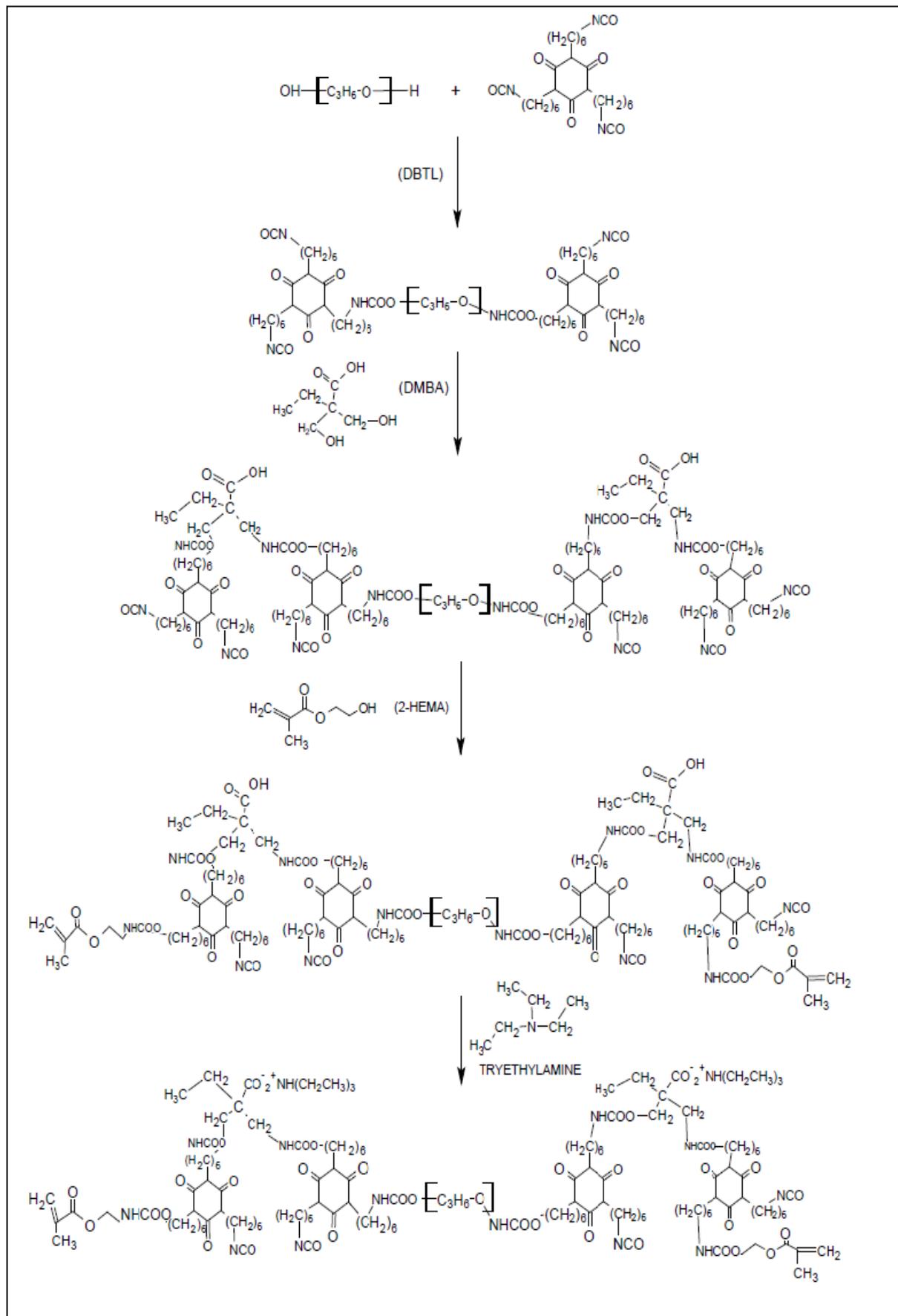


Figure 1. The synthetic route of the UV-WPUA oligomer.

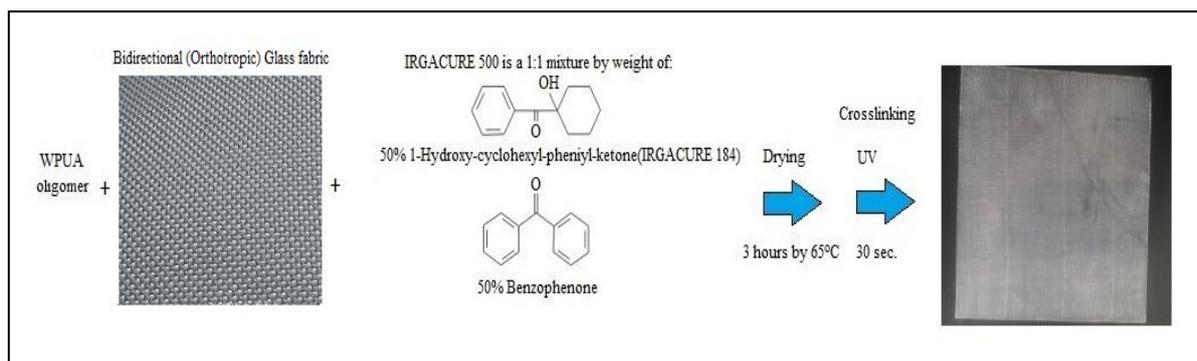


Figure 2. Preparation of UV-curing fiberglass composites.

Mechanical properties of UV-curing fiberglass composites

Tensile strength testing and elongation at break testing for all of the specimens were carried out on „Zwick Z 020” Zwick GmbH & Co. KG, Ulm, Germany at room temperature at a speed of 50 mm/min. All measurements had an average of three runs. The dumbbell-type specimen was prepared according to EN ISO 527-3:1995.

Fibre and matrix volume of the composites

Fibre volume ratio is easily determined by simple weighing of a defined area of the composite of known glassfiber mass. Typically, an ASTM D3171-15 test method is employed which requires weighting of the sample and knowledge of the density of the components. The resin volume is the difference between the composite and fibre volume and was calculated according to the following formula:

$$V_{fiber} = V_{composite} - V_{matrix}$$

Thermal properties of fiberglasses (DSC)

Differential scanning calorimetry (DSC) of the UV-cured fiberglass composites were performed on a „DSC 204 Phoenix”, NETZSCH, Germany according to ISO 11357. The programmed heating range was from -100°C to 300°C at a heating rate of 10 °C/min under a nitrogen atmosphere. The measurement was performed at with 6–10 mg samples. DSC curves were recorded.

RESULTS AND DISCUSSIONS

Particle size of oligomers

The results from particle size determination are presented at Figure 3 and Figure 4. For WPUA average size is 145 [d.nm] in comparison with Bayhydrol 2317 at about 88, 40 [d.nm]. These strong difference between polyols will affect not only at the physical properties of the

polyols and also of the mechanical properties of the fiberglass samples.

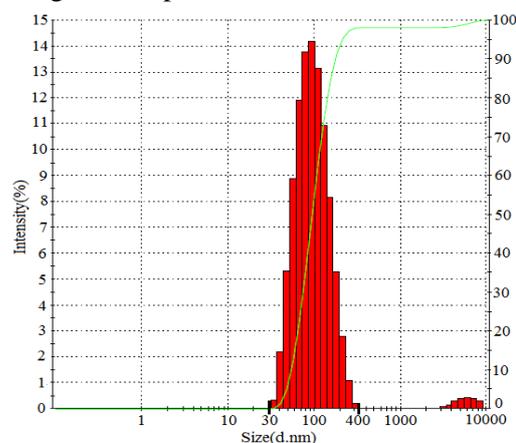


Figure 3. Particle Size of Bayhydrol 2317.

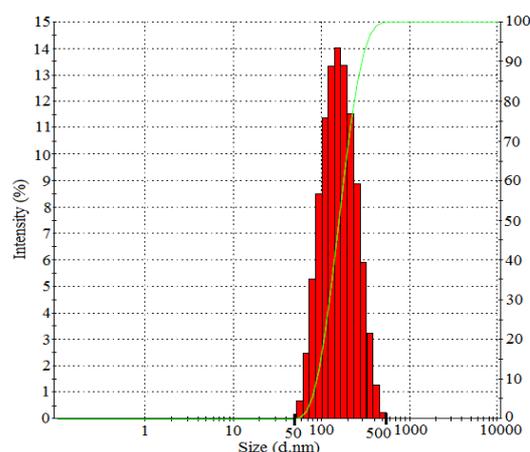


Figure 4. Particle Size of WPUA oligomer.

The apparent viscosity of WPUA oligomers

It can be observed at Figure 5, that there is a difference in viscosity between WPUA and Bayhydrol 2317 and WPUA oligomer is preferable not only as a matrix in fiberglass composites and also for a spraying method because of its lower viscosity.

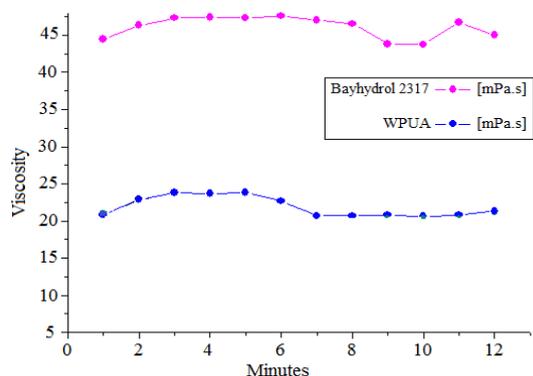


Figure 5. Viscosity of WPUA oligomer.

IR spectra of the matrix

The FTIR analysis at Figure 6 was used mainly to check the completeness of the polymerization reaction, in terms of the disappearance of the NCO band at 2255 cm^{-1} and the appearance of the N-H band at 3362 cm^{-1} . The result indicated that the NCO had reacted with OH into NHCOO and the NCO groups had been completely bonded. Besides the presence of a band at 1682 cm^{-1} is characteristic for the urethane group C=O and the band at 1531 cm^{-1} belongs to C-NH group from the urethane. The strong bands at 2970 , 2863 , 1462 and 1373 cm^{-1} are C-H asymmetric and symmetric vibration, as well as asymmetric and symmetric stretching CH_3 .

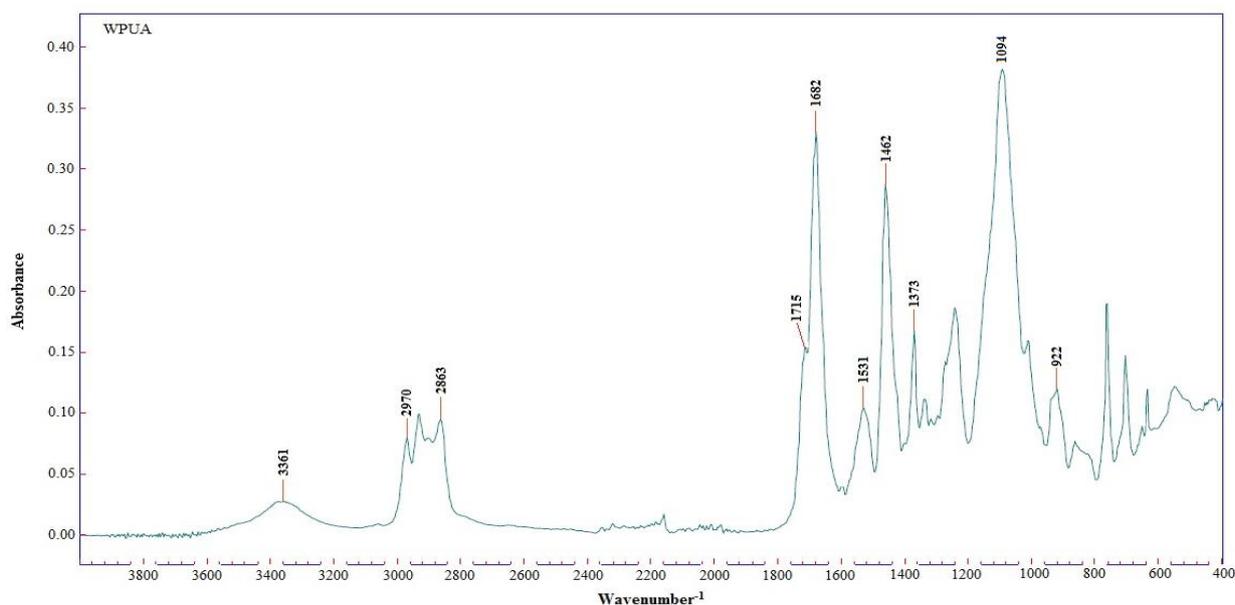


Figure 6. IR spectra of the matrix.

The FTIR spectrum of the matrix: There is a wide peak at 3375 cm^{-1} , which belongs to the OH groups from 2-HEMA (used by oligomer synthesis). The peak at 1715 cm^{-1} peak is characteristic for the carbonyl group (C=O), and 2-HEA. The peak at 1094 cm^{-1} belongs to the (C-O) bond. The intensity decrease of the peak at 922 cm^{-1} is a polymerization result, whereas the double bond ($\text{CH}_2=\text{CH}$) in the acrylate moiety breaks.

Thermal properties of fiberglasses (DSC)

The DSC curves of the WPUA fiberglass composites are shown in Figure 10. From which, it can be seen that the samples (1-3) have one glass transition temperature, around 21 , 24 , 30°C and exothermal peaks at about 160°C which is a symbol of reactivity after the UV-curing, expecting affects to the mechanical properties of the samples. The conclusions from the abovementioned results are, that it is recommended not only UV light and also temperature treating for the fully completion of the curing.

Fibre volume of the composites

It can be observed from Table 1, that the fiber volume fractions of the samples ranged from $50,61\%$ to $69,52\%$.

Table 1. Composite fibre and matrix volume

Sample	Matrix	Fiber grammage	V _{fabric}	V _{matrix}
1	WPUA	81 g/m ²	61,84%	38,15%
2	WPUA	163 g/m ²	50,61%	49,38%
3	WPUA	660 g/m ²	69,52%	30,47%

Mechanical properties of UV-curing fiberglass composites

It can be observed in general from Figure 7- 9, that optimal elongation at break properties was observed in sample 1 glassfiber reinforced

composites with glass fabric weight- 660 g/m², optimal tensile strength and minimal Young’s modulus by sample 2 glassfiber reinforced composites with glass fabric weight- 163 g/m².

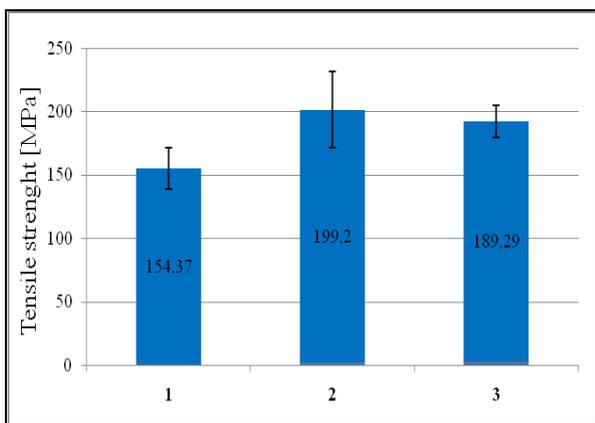


Figure 7. Tensile strength of fiberglass composites.

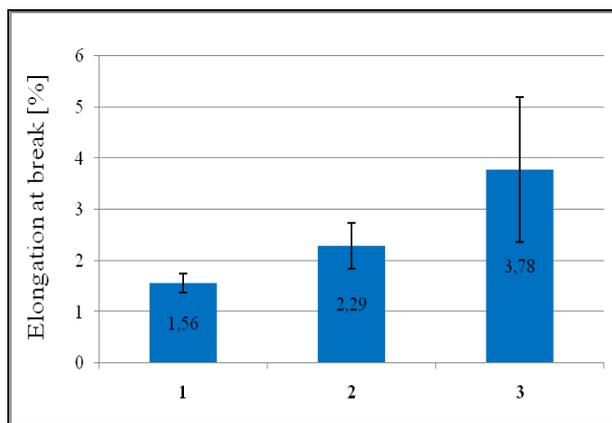


Figure 8. Elongation to break of fiberglass composites.

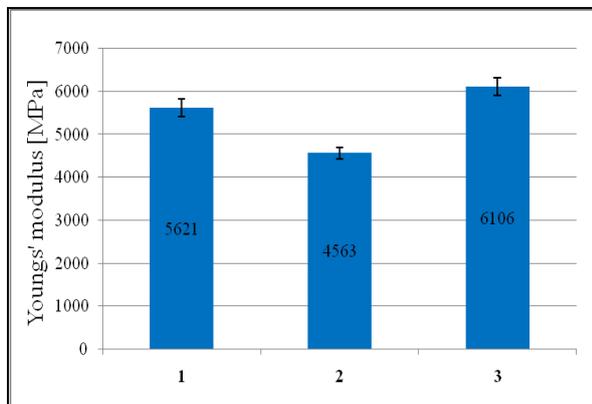


Figure 9. Young’s modulus of fiberglass composites.

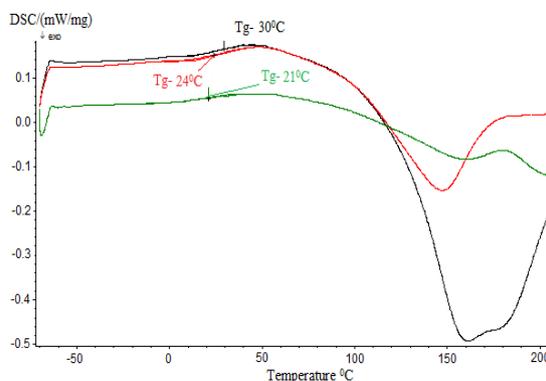


Figure 10. DSC curves of the composites

SUMMARY

The samples were prepared using UV-PUA oligomer, the Irgacure 500 and the monomer 2-HEA. The quantity of 2-HEA, the content of the Irgacur 500, the drying time of the samples, the temperature and the curing time have important effects on the properties of the UV-cured fiberglasses. The experimental results indicated that the optimum irradiation time was 30- 50s after the UV-PUA being applied on a poly (tetrafluoroethylene) -“TEFLON” plate at room temperature, and catalyst (photoinitiator) dosage was 4% (wt%) of the total amount. Almost all the

UV-cured fiberglasses have a residue bonds and that will be a topic for additional investigations. The UV-curing PUA dispersions are especially advantageous in high production open molding, pultrusion and filament winding processes for many different products and their quick fix, such as boats, skylight panels, shower and tub enclosures, RV and truck panels, poles, tanks, pipes. Manufacturers of these and other products should evaluate photocuring as a way to increase production and lower styrene emissions.

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ИЗГОТВЯНЕ, СВОЙСТВА И ПРИЛОЖЕНИЕ НА ВОДОДИСПЕРГИРАН ПОЛИУРЕТАН-АКРИЛАТЕН ОЛИГОМЕР КАТО МАТРИЦА ЗА УВ-ВТВЪРДЯВАЩИ СЕ СЪТЪКЛОПЛАСТИ

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Постъпила на 18 октомври, 2016 г.; приета на 12 февруари, 2017 г.

(Резюме)

Изготвен е вододиспергиран полиуретан- акрилатен олигомер -(ВПУА) чрез анионен самоемулсифициращ метод от Хексаметилен диизоцианат (ХДИ), полиетер полиол (Лупранол 1000/1), диметилбутанова киселина (ДМБК), и се въвеждат акрилатни крайни групи с 2-хидроксиетил метакрилат (2-ХЕМА). След което е получен стъклопласт втвърдяващ се след облъчване с ултравиолетова (УВ) светлина от ВПУА олигомер, реактивен разтворител 2-хидроксиетил акрилат (2-ХЕА), фотоинициатор Иргакюр 500 и стъклени платове с различно тегло (81, 163, 660г/м²). Изследвани са физичните свойства на произведените ВПУА олигомери чрез Инфрачервена спектроскопия, определен е размерът на частиците и вискозитетът. Определени са механичните свойства на УВ-втвърдяващите стъклоусилени композити- якост на опън, удължение при скъсване, и термичните свойства чрез ДСК (диференциално сканираща калориметрия). Специфичните УВ-ВПУА са материали с широка област на приложение. Получените резултати определят изготвеният УВ-ВПУА като подходящ за матрица на УВ- втвърдяващи се композити.