AN INVESTIGATION ON THE POSSIBILITY OF FIBERGLASS MANUFACTURE USING A MATRIX OBTAINED FROM WATER DILUTED MIXTURES OF UNSATURATED POLYESTER AND POLYURETHANE RESINS

Andrey Matev1, Petar Velev1, Michael Herzog2

1 University of Chemical Technology and Metallurgy
8 Kliment Ohridski, Sofia 1756, Bulgaria
E-mail: p_velev@uctm.edu
2 Technische Hochschule Wildau TH- Wildau
Wildau 15745, Germany

ABSTRACT

Four types of matrices obtained from a mixture of unsaturated polyester resins diluted by water and a water-dispersible polyurethane-acrylate oligomer (Bayhydrol® UV 2317) of different percentage (20 %, 40 %, 60 %, 80 %) are used for production of glass reinforced composites. Then composites are obtained from the matrices mentioned above and glass fabric of a weight of 81 g/m² and 163 g/m². The physical properties of the composites prepared are investigated by ATR-FTIR. Some mechanical properties, such as tensile strength, elongation at break and thermal properties of the composites are measured. Specific matrices are selected as they are suitable for composites preparation. The latter can be used for fiberglass production. Future study is required aiming to decrease the styrene emissions during lamination and curing.

Keywords: fiberglass composites, unsaturated polyester resin, waterborne polyurethane-oligomer, mechanical properties, thermal properties.

INTRODUCTION

The glass fibers are the most used reinforcement in the manufacturing of composite materials with polymeric matrices. The matrix of the composites is composed of organic, thermostable polyester, vinyl ester, phenolic or epoxy resins. Polyester resins make up some 75 % of these matrices [1]. The widespread use of these oligomers is due to their relatively high physical and mechanical indicators as well as their relatively low cost. The hardened unsaturated polyester resins show fragility and susceptibility to crazing which are significant shortcomings. They result from internal tensions determined by the volumetric shrinkage in the process of cross-linking. The unsaturated polyesters can be modified by introducing polyurethane oligomers. This is an opportunity to improve the properties of the fiberglass produced on the ground of a matrix of unsaturated polyester resin [2]. Polyurethanes (PUs) are used in extensive fields of commercial applications. They are also unique polymeric materials with a wide range of physical and chemical properties [3, 4].

The unsaturated polyester resin can be diluted with water as the polymerization (curing) is carried out in presence of water. Dilution to 50 % content of unsaturated polyester resin provides better distribution of the bulky fillers [5].

Polyurethanes based on water are becoming more popular because of their excellent mechanical properties and good fire resistance. They are also environmentally friendly [6]. The cross-linking of these polyurethanes taking place in presence of ultraviolet light proceeds with a low power consumption gives a product of high chemical stability [7, 8].

Conditions providing self-crosslinking can be set up in a pre-stirred mixture of polyurethane and unsaturated polyester resin. This results in the formation of interpenetrating polymer networks. A product of a high degree
of crosslinking [9] is obtained.

In this study UV-cured waterbased polyurethane is a component of a mixed matrix. The aim is to investigate the possibility of using the latter to produce composite glass fibers materials.

EXPERIMENTAL

Materials
The materials used in this refer to:
• WPUA 2317 with the trade name Bayhydrol® 2317 (this is an urethane acrylate dispersion provided by Bayer Material Science AG, Leverkusen, Germany);
• Unsaturated polyester resin DISTITRON® 429® and methyl ethyl ketone peroxide-MEKp (products of NMS-Faserverbundwerkstoffe, Bad Laer, Germany);
• IRGACURE 500® (a liquid mixture of two photoinitiators, a product of BASF, Germany);
• Silane coated by glass fabrics with a weight of 81 g/m² and 163 g/m² (produced by XP- Textiles GmbH).

The initial compositions used to obtained glass fiber composites are presented in Table 1.

Preparation of fiberglass composites based on a mixed matrix
The fiberglass composites were prepared by casting unsaturated polyester resin 429. A few drops of ammonia were added under stirring to provide the mixing with Bayhydrol 2317. Then the hardener MEKP and IRGACURE 500 were added. The homogeneous mixture obtained was deposited on glass fabrics and dried at 80°C for 10 min. Crosslinking activated by MEKP proceeded during this stage. The water was used to dilute the WPUA system was removed through evaporation prior to the UV-curing. Then UV-irradiation was applied for 30 s using a lamp (the main wavelength referred to 365 nm, the lamp power was equal to 400 W, the UV emission was equal to 1200 mW/m², while the distance between the sample and the lamp center was 10 cm). Irgacure 500 was activated providing the polymerization radicals required. The latter attacked the acrylate double bonds of the monomers and the oligomers forming polymers.

Characterization techniques
Fiber volume ratio
The fibre volume ratio was determined by weighing a defined area of the composite of a known glass fiber mass. The ASTM D3171-15 test method was applied. The fiber volume was estimated as a difference between the volume of the composite and that of the matrix, i.e. $V_{\text{fiber}} = V_{\text{composite}} - V_{\text{matrix}}$.

Structure characterization of ATR-FTIR matrix
The attenuated total reflection (ATR) spectrum of the matrix was obtained according to ASTM E1252, a

<table>
<thead>
<tr>
<th>Sample N</th>
<th>Weight of the glass fabric, g/m²</th>
<th>DISTITRON® 429, m %</th>
<th>Bayhydrol® UV 2317, m %</th>
<th>Harder-MEKp m %</th>
<th>IRGACURE® 500, m %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>81</td>
<td>81,43</td>
<td>16,29</td>
<td>1,63</td>
<td>0,65</td>
</tr>
<tr>
<td>2</td>
<td>81</td>
<td>69,65</td>
<td>27,85%</td>
<td>1,39</td>
<td>1,11</td>
</tr>
<tr>
<td>3</td>
<td>81</td>
<td>60,83</td>
<td>36,50</td>
<td>1,22</td>
<td>1,45</td>
</tr>
<tr>
<td>4</td>
<td>81</td>
<td>53,99</td>
<td>43,20</td>
<td>1,08</td>
<td>1,73</td>
</tr>
<tr>
<td>5</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>98</td>
<td>96</td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>163</td>
<td>81,43</td>
<td>16,29</td>
<td>1,63</td>
<td>0,65</td>
</tr>
<tr>
<td>8</td>
<td>163</td>
<td>69,65</td>
<td>27,85</td>
<td>1,39</td>
<td>1,11</td>
</tr>
<tr>
<td>9</td>
<td>163</td>
<td>60,83</td>
<td>36,50</td>
<td>1,22</td>
<td>1,45</td>
</tr>
<tr>
<td>10</td>
<td>163</td>
<td>53,99</td>
<td>43,20</td>
<td>1,08</td>
<td>1,73</td>
</tr>
<tr>
<td>11</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>
standard practice for general ATR-techniques for obtaining infrared spectra for a qualitative analysis between 4000 cm\(^{-1}\) and 400 cm\(^{-1}\). A FT-IR spectrometer (Varian 620-IR, FT-IR) was used. A minimum of 256 scans were recorded and the results were averaged. The resolution was equal to 2 cm\(^{-1}\) in the range studied.

**Composites thermal properties**

Differential scanning calorimetry (DSC) of the UV-cured fiberglass composites was performed on DSC 204 Phoenix (NETZSCH, Germany) following the requirements of ISO 11357. The programmed heating range was from -100°C to 300°C at a heating rate of 10°C/min. Nitrogen atmosphere was used. The samples studied had a mass of 6 mg - 10 mg.

**Mechanical properties of UV-cured fiberglass composites**

Tensile testing of all specimens were carried out on a tensile tester Zwick Z 020 (Zwick GmbH & Co. KG, Ulm, Germany) at room temperature at a speed of 2 mm/min for E-module determination and of 10 mm/min for the rest of the tests. All measurements were three times. The dumbbell-type specimen was prepared according to EN ISO 527-3:1995 (ASTM D3039).

**3D microscope**

Optical microscopy was applied to obtain a qualitative image of the fiber packing, arrangement, and porosity in the composites. A morphological analysis was also carried out to determine the wetting ability of the composites hybrid matrices. A digital microscope VHX-600 (Keyence Co., Canada) was used.

**RESULTS AND DISCUSSION**

**Fiber volume content**

The filler amount in the samples, measured as a percentage of the sample volume is presented in Table 2. The change in the volume ratio between the polymer matrix and the reinforcing component is due to the evaporation of water from the polymer matrix in the process of drying. This water comes from the water-dispersible polyurethane-acrylate, and hence it is of a different amount in each composition (depending on Bayhydrol® UV 2317 input). The drying process, which leads to a reduction of the volume of the polymer layer, affects also the quality of the sample surface.

**Matrix structure characterization by ATR-FTIR**

The peak at 1715 cm\(^{-1}\) shown in Fig. 2 is characteristic of the carbonyl group (C=O). The peaks at 1150 cm\(^{-1}\) - 1000 cm\(^{-1}\) refer to the (C-O) bond. There is intensity decrease of the peak at 923 cm\(^{-1}\) resulting from polymerization, whereas the double bond (CH\(_2\)=CH) in the acrylate moiety breaks. The consumption of styrene
monomer is followed by the area change of the peak at 912 cm\(^{-1}\), while C=C bond consumption in the unsaturated polyesters is followed by the area change of the peak at 982 cm\(^{-1}\). The styrene and polyester C=C bonds can be easily determined on the ground of the changes of the peaks at 912 cm\(^{-1}\) and 982 cm\(^{-1}\), respectively. These peaks decrease in the course of curing. They can even shift to 890 cm\(^{-1}\) and 978 cm\(^{-1}\), correspondingly [10].

**Thermal properties of fiberglass**

The DSC curves of the fiberglass composites are shown in Fig. 3. It is well recognized that polyurethanes have two-phase morphology resulting from the hard segment phase separation. The copolymer composition, the block length, as well as the inter- or intra-molecular interactions affect the extent of phase separation [11]. It can be seen that two glass transition temperatures (T\(_g\)) are outlined are outlined in the DSC curves. They refer to the ranges of 12 °C - 21°C and at 58°C - 66°C. They are indicative of the soft and hard segments presence in the polyurethane or of the fact that the mixed matrices components are immiscible. Fig. 3 shows no endothermic peaks in the range of 100°C-120°C. This indicates that the WPUA water in the mixed matrices is evaporated. The isothermal curves of the samples containing 20 % and 40 % WPUA visualize the high mobility of the polyester and styrene C-C bonds as the conversion is not complete.

Variable data on the thermal stability of polyurethanes and polyurethane-urea materials is found in the literature. This is due to the wide variety of systems that can be synthesized using isocyanate, polyol, curing agents and chain extenders. The initial thermal decomposition of polyurethane elastomers is in the range of 110°C to 270°C depending on the composition and the method of analysis. The urethane bond is relatively unstable and its dissociation occurs between 150°C and 220°C [12]. The initial decomposition temperature observed in case of all samples studied is above 250°C. Furthermore, the systems have good thermal stability.

**Mechanical properties of UV-cured fiberglass composites**

Fig. 4 presents the results referring to the tensile strength and elongation at break of the composite ma-
The data shows that the composites containing 60% of WPUA in the matrix and glass fabric of 163 g/m² have the highest values of the tensile strength at about 320 MPa. This result can be explained with the best wetting properties of the resin. The composites containing 80% of WPUA have low tensile strength values at about 180 MPa for the sample of a glass fabric mass of 81 g/m² and at 260 MPa for the composite reinforced with glass fabric of a weight of 163 g/m². This observation is explained with the high quantity of polyurethane-acrylate and water in the resin.

The optimal values of elongation at break are obtained in case of a sample containing 60% of WPUA in the mixed matrix and glass fabric of a weight of 163 g/m² and that containing 60% of WPUA and glass fabric of a weight of 81 g/m². They are equal to 6.9% and 4.3%, respectively. The results referring to the elasticity modulus...
(Young’s modulus, MPa) of the composite materials obtained are shown in Fig. 4. It is clearly visible that those containing 80% of WPUA have the lowest modulus of elasticity. This is due to the lowest stiffness of the polymer matrix as a result of the highest WPUA quantity and 0.05%-0.25 % stretching of the bidirectional glass fabrics. The highest values of the elasticity modulus are obtained for composites containing 40 % of WPUA and glass fabric of 81 g/m² and of 163 g/m². They are equal to ca 5.8 GPa and 4.3 GPa, correspondingly.

3D microscope

The microscopic images of the surface structure provide visualization of the objects studied [13]. The SEM results are shown in Fig. 5. It can be concluded that the glass fibers amount in the mixed Bayhydrol® matrices does not affect the quality of the glass fabric wetting.

CONCLUSIONS

Samples containing glass fabrics of a weight of 81 g/m² and 163 g/m² and polymer matrices composed of an aqueous dispersion of an unsaturated polyester resin and Bayhydrol® in different ratios are prepared. The experimental results obtained show that the amount of Bayhydrol®, which is directly related to the amount of water in the matrix, affects all composite materials properties studied. It can be assumed that the optimal quantity Bayhydrol® in the polymer matrix refers to ca 60 %. The deterioration of the physical and mechanical properties of composites containing a matrix of a higher Bayhydrol® content is probably due to the presence of excessive amount of water in the system, which impedes the formation of interpenetrating polymer networks through its effect on the kinetics of oligomers the crosslinking. The DSC analysis results verify that the cross-linking of the unsaturated polyester resin is incomplete. It can be expected that the properties of the composite materials can be improved through cross-linking agents’ optimization.

The materials produced do not show the best mechanical properties but they have a potential in respect to solidification of the matrix, styrene emission reduction and quick repairs workability.

REFERENCES

5. M. Natov, P. Velev, Suspension copolymerization of unsaturated resins with styrene and acrylonitrile, Macromolecular chemistry and physics, 201, 12, 2000, 1244-1249.


