

# COATINGS FOR IMPROVED ADHESION STRENGTH AND RESISTANCE OF GLASS CORD

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## 1 Introduction

Polymer matrix composites are tailorable materials, due to valuable properties, like increased mechanical strength and improved barrier properties of gasses and liquids, enhanced resistance towards aggressive media exposure. Considerable improvement can be achieved by improved matrices, high performance reinforcement and improved fibre/matrix interphases [1, 2]. A particular example and one of the most interesting cases out of the variety of possible material combinations of high-performance reinforcements can be glass fibres or glass cords [3, 4]. The use of glass cord is perspective due to beneficial combination of mechanical properties of glass fibres and elastic properties of polymers, especially in the case of rubbers. For example, glass fibre/rubber composites are used in automotive industry as a component of timing belts.

The adhesion strength between all constituents of fibre/rubber composite determines the set of macroproperties of the material. Despite numerous achievements in the field of fibre/rubber composites [2, 4] the issue of mutual component bonding in a composite is still under consideration [5], but most of scientists' attention is focused on synthetic fibres, such as nylon, polyester or rayon fibres, but the case of glass fibre/rubber composites represents a set of almost untouched questions. In this case adhesion behaviour should be more complicated due to both unique geometry and chemical composition of the composite. Unfortunately, investigations are practically absent in this field except the work of Stevens *et al.* [6].

It is also highly challenging to improve the environmental durability of coated glass fibres [7, 8]. There is a huge amount of various attempts to investigate and to increase resistance of glass fibre/polymer composites, using various kinds of polymers, such as epoxy resins [9-14], vinyl- [15-19] and polyesters [20-22], as well as particular perspective polymers as polycarbonate [23], polyethylene- (or polybutylene- [24]) terephthalate

[25, 26], polysulfone [27], including even such exotic mixtures as bamboo fibre reinforced polypropylene composite and bamboo/glass fibre reinforced polypropylene hybrid composite [28]. Some of these trials are quite successful and provide almost zero composite degradation after aggressive media exposure [23]. Unfortunately, the proposed solutions are far away from an industrial approach of glass fibre processing.

The E-glass fibres mostly used are known to have a low hydrolysis or corrosion resistance. In alkali or acidic media the use of special chemical resistant glass fibres, e.g. alkali resistant (AR-), chemical stability (C-) or corrosion resistant glass fibres (ECR)) is recommended. Parts containing special corrosion resistant glass fibres had longer times to failure in comparison with samples containing E-glass fibres. Nevertheless E-glass is the most popular component of glass fibre/polymer composites due to its price/performance ratio. Therefore, the increase of its durability is highly desirable.

Despite the vast accomplished experimental work it can be concluded that there is a lack of data and no systematic description or fundamental aspects (e.g. relationship surface properties and durability) for glass fibre/rubber composites to prevent environmental influence on the one hand and to provide the excellent interfacial adhesion on the other hand, and therefore further profound systematic investigation in this field is needed.

Taking into account good barrier properties of polymers it seems very attractive to use water-based polymer coatings in order to improve environmental durability of glass fibres caused by healing of critical surface flaws and improved interfacial interaction.

The main objective of this work is the investigation of glass cord/rubber composites influenced by both the material structure varied by the chemical composition of both glass formulation and sizings/nanocoatings contents. The reactive polymeric mixtures will be modified with

nanoparticles avoiding environmental unfriendly components like widely used formaldehyde. The main tasks are interphasial behaviour studies of glass cord sizing and coating in order to explore the mechanisms for enhanced adhesion strength and improved environmental durability of such high-performance rubber composites aimed at use in the automotive industry.

Physico-chemical methods' combination and the opportunity to vary systematically the composition of the glass fibre/rubber composites will provide a deeper insight into interface formation in such structures.

## 2 Experimental part

### 2.1 Materials

E-glass fibres (GF) have been made at the Leibniz Institute of Polymer Research Dresden by using a continuous pilot plant spinning equipment [3]. The filaments are sized within the continuous spinning by various sizings consisting of silane coupling agents, 3-glycidoxypropyltrimethoxysilane, and 3-mercaptopropyltrimethoxysilane, as well as of their mixtures in conjunction with film formers based on epoxy resins in the aqueous sizing. Aqua ternary ammonium surfactant and a non-ionic surface-active agent were added to the emulsion for homogeneous dispersion of the constituents.

After spinning the yarns (204 single filaments, 9  $\mu\text{m}$  diameter, 34 tex yarn fineness) were dried at 120°C for 6 hours in an oven and after that the polymer coating (or dip) was applied, which consists of the prematured resorcinol-formaldehyde resins (RFL; Penakolite R50 (Castle Chemicals Ltd, Peak House, United Kingdom) and Askofene 779W50 (ASK Chemicals, Hilden, Germany)) mixed with styrene butadiene (SB; trade name Nipol LX112; Zeon Corporation, Tokyo, Japan), and acrylo-nitrile (AN; 31.5-33.5% of the bound acrylo-nitrile groups, trade name Nipol 1562; Zeon Chemicals Europe Limited, Sully, United Kingdom) nanodispersions (SB: non-carboxylated, Tg: -52°C, particle size: 100 nm; AN: Tg: -29°C, particle size: 70-90 nm) with or without carbon black (CB; trade name Derussol Z35; Evonik Degussa GmbH, Hanau, Germany) nanodispersion (particle size: 167 nm) of 35 wt%. The dipping and fast infrared drying after (drying speed 4 m/min at 250°C) has been applied using continuous coating system HVF/KTF with infrared pre-dryer (Mathis AG, Switzerland).

The chemical composition of the polymeric mixture used for GF coating was varied by RFL and polymer latex (SB and AN) ratio in order to replace RFL in

steps. The total weight gain due to the coating ranges from 10 up to 20 wt% determined by pyrolysis (600°C for 60 min) of the coated fibres.

As a matrix peroxide-cured hydrogenated nitrile-butadiene rubber (HNBR; Gates GmbH) was used. Embedding of coated glass yarns into the matrix and further vulcanization of rubber block was carried at 170°C under pressure 150 kN for 30 min using table press TP 1000 (Fontijne Grotnes, Holland).

To determine hydrolysis resistance or environmental durability of the produced coated E-glass fibres, a simple so-called "boiling test" was used. The coated glass fibres were exposed to hot distilled (98°C) water for 4 hours. After boiling test glass fibres were dried at room temperature for 48h.

For comparison purposes, coated GF supplied by Volkswagen Group and sized GF of Saint-Gobain Vetrotex have been used as reference commercial fibres. This roving has a fineness of 108 tex and an average filament diameter of 9  $\mu\text{m}$ .

### 2.2 Characterization methods

Adhesion strength as pull-out force value between HNBR and the various developed polymer coatings has been tested according to ASTM D 2229-85 (so called T-Test or pull-out test) using the universal testing machine Zwick Z010 (Zwick, Ulm, Germany) with a deformation velocity of 20 mm/min.

Yarn and roving tensile strength tests before and after boiling test have been performed using the tensile testing machine Zwick Z100 (Zwick, Ulm, Germany) with a deformation velocity of 200 mm/min. Cable clamps for the specimens have been used to avoid slipping and fibre fatigue because of high contact pressure in the specimen holders. Optical sensors were used for a direct elongation measurement. The error bars in all the figures of this work represent the standard deviation of the measurements. In the case of tensile strength measurements standard deviation was around 100 MPa.

Glass transition temperatures of both used raw/initial polymer materials and final polymeric mixtures for the coating were measured by differential scanning calorimetry (differential scanning calorimeter Q2000, TA Instruments, USA) in the temperature range from -80 up to 200°C under a nitrogen atmosphere at a heating rate of 10 K $\cdot\text{min}^{-1}$ ; the weight of the fibre samples was 1.6 - 5.5 mg. For the precise calculation of glass transition temperatures the first derivative of a thermogram was used in every case.

To control the surface quality of polymer coatings before and after pull-out tests scanning electron microscopy was used. SEM images have been obtained by scanning electron microscope LEO 435 VP (LEO Elektronenmikroskopie GmbH, Germany) and Scanning Electron Microscope Ultra Plus (Zeiss, Germany).

### 3 Results and Discussion

#### 3.1 Adhesion strength

To evaluate the adhesion strength between rubber matrix (HNBR in our case) and the developed polymer coatings, the T-Test or pull-out test (pull-out force of the yarn from a rubber block as a measure of adhesion strength between composite constituents) has been carried out. Fig. 1 presents the results of pull-out tests. The pull-out force of control sample (the industrial cord of Volkswagen Group) is given by the dashed line. Chemical composition and physico-chemical structure of the polymer coating network within the composite has been varied as a function of polymer latex mixtures (SB/AN ratio, no CB, Fig. 1a, open squares) and cross-linking agent concentrations as formaldehyde-resorcinol ratio (F/R ratio, Fig. 1b). The functionality and pull-out force correspondingly decreases with increasing of SB's concentrations in polymer coatings and one can expect a decrease of pull-out force, as SB's fraction in coating increases. However, the pull-out force curve has two maxima, that are corresponding to 50:50 ratio of SB and AN, as well as to the pure AN, as it can be expected for affinity reasons. A probable explanation of the second maximum (SB/AN = 50/50) can be the glass transition temperature value ( $T_g$ ) of the developed coatings (see Fig. 2a). An equal amount of AN and SB (50%) in the coating structure provides the lowest possible  $T_g$  (-53°C) with the highest functionality in comparison with other states (of higher SB's amount), therefore such a state can provide the best materials interlocking what results in the highest pull-out force values.

The insertion of inorganic particles (CB; Fig. 1a, black square) into a polymer coating increases pull-out force of glass fibre/polymer composites up to 33% in comparison with the case without CB.

The degree of cross-linking (F/R ratio in our case) influences adhesion between components in the composite [29]. Eco-unfriendly behaviour of formaldehyde is well-known as well; nevertheless the usual industrial F/R ratio in RFL systems is rather high (about 1.4-1.5). It is interesting that the optimum level of F/R ratio for such systems given in literature is 2 [29] and is valid for a mixture of pure

components, but the available dip formulation using so called "prematured" resorcinol-formaldehyde resin is 1.7. The higher F/R ratio results in complete dip hardening.

The accomplished experiments showed that similar or beneficial, up to 41% improved pull-out force values in comparison with control sample, can be reached at lower F/R ratios (Fig. 1b). To find an optimal level of polymer network, the dips with various F/R ratios were prepared and tested using commercially available resin Penakolite. The optimal point of F/R ration was clarified at 1.02.

The results of T-test are in a good agreement with the values of glass transition temperature for polymer coatings with various F/R ratio (Fig. 2b). As Fig. 2b shows the minimum of glass transition temperature is corresponding to the same optimum point as it was in pull-out test results – 1.02. Similar to the previous case one can say that in this point flexibility of polymer chains and therefore their mechanical interlocking is the highest one.

The problem of a prematured resin is the various producers use a different initial quantity of formaldehyde and resorcinol to prepare a prematured resin (Penakolite – 0.55, Askofene – 0.60). The addition of the same amount of formaldehyde into the dip formulation as it was in the case of formulation with Penakolite resin, but using the resin of other producer (Askofen), gives the lower pull-out force value (Fig. 1b, the open circle). If one recalculates the necessary amount of formaldehyde to attain the obtained optimal F/R ratio value taking into consideration producer's recipe (namely, initial F/R ratio of a prematured resin), the same adhesion level (41% higher than the control sample) is reached again (Fig. 1b, the open triangle (pseudo Penakolite)). It shows the obtained value is universal and depends only on chemical composition of a used prematured resin.

The SEM images (Fig. 3) of dip surfaces before and after pull-out test confirm results of pull-out test. The initial state of dip surface (Fig. 3a) is rather smooth and homogeneous in all cases. After pull-out test (Fig. 3b), a significant amount of bonded rubber material characterizes the dip surface. This result is in a good agreement with high pull-out force values.

#### 3.2 Environmental durability

Losses of mechanical strength for the commercial GF are 50% at the initial tensile strength of about 1.7 GPa (see Table 1). Improved mechanical properties and resistance, e.g. environmental durability, of the whole glass fibre (cord)/polymer composite are

determined by the sufficient adhesion between the rubber and the polymeric fibre coating. As it was expected, an enhanced level of environmental durability was achieved taking into account the results of pull-out tests and using the obtained beneficial chemical compositions (for the maxima of the pull-out force). The maximum of tensile strength values of dipped fibres is in a good agreement with results of T-Test and is corresponding to F/R = 1.02 and pure AN in dip formulation (compare dips with and without SBR, Table 1). It can be also concluded that the affinity of chemical composition plays the more important role in mechanical interlocking of materials than glass transition temperature of a used polymer. On the other hand insertion of SBR enhances the durability of the composite and the mechanical losses after boiling slightly decrease. The insertion of inorganic CB-particles (see the Table 1) into the polymer coating results in higher hydrolysis resistance rate what is in a good agreement with other published works [1, 3]. CB particles provide an additional obstacle for water and hinder water diffusion process through the polymer film on the glass surface. As a result the obtained values of tensile strength losses after boiling test compared with initial tensile strength for the developed samples are only 11-15% and 2 GPa, respectively.

#### 4 Conclusions

Novel polymer coating formulations of high durability and adhesion strength to HNBR substrate have been developed. The optimal values of both polymer latex- and F/R ratio driving adhesive and mechanical properties of the polymer finish have been determined.

The optimum of F/R ratio is shown to be an universal value and depends only on chemical composition (F/R ratio) of a prematured formaldehyde-resorcinol resin. The comparable or beneficial values of adhesion strength (pull-out force; benefit is up to 41%) at lower formaldehyde content in dip formulations have been obtained.

The glass transition temperatures, which characterize flexibility of polymer chains or mechanical material interlocking of polymer mixture for all coatings are in a good agreement with results of pull-out tests. One can conclude that  $T_g$  is one of the driving factors which determines adhesive properties of polymer coating. The best polymer latex ratio as well as F/R ratio in the dip formulation are corresponding to the minima of  $T_g$ . On the other hand chemical affinity of the constituents and the

chosen substrate determines the adhesion behaviour as well and can play an even more important role than physical network due mutual penetration of polymeric chains at interface.

The tensile strength of the developed fibers as well as their tensile strength loss (only 10-15%) after the boiling test as a measure of environmental durability of GF is determined by an adhesion strength between components of glass fiber/rubber composite and the measured values are in a good agreement with results of the pull-out test.

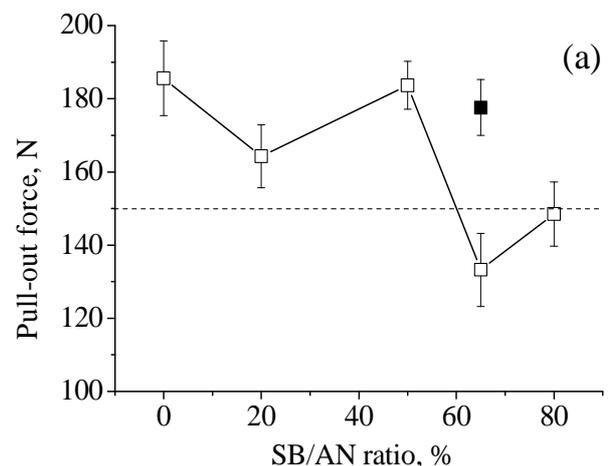
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Table 1. Dependence of tensile strength values of developed samples on chemical dip composition.

| Dipped Glass Fibers<br>(dip type)          | Tensile strength, MPa |         |
|--|-----------------------|---------|
|  | before                | loss, % |
| Reference<br>(see Experimental part)       | 1667                  | 50      |
| ANR dip without CB                         | 2082                  | 40      |
| ANR/SBR dip without CB                     | 1903                  | 38      |
| ANR/SBR dip with CB                        | 2008                  | 29      |
| ANR/SBR dip with CB<br>(the optimal ratio) | 2020                  | 15      |
| ANR<br>(the optimal F/R ratio)             | 1911                  | 11      |



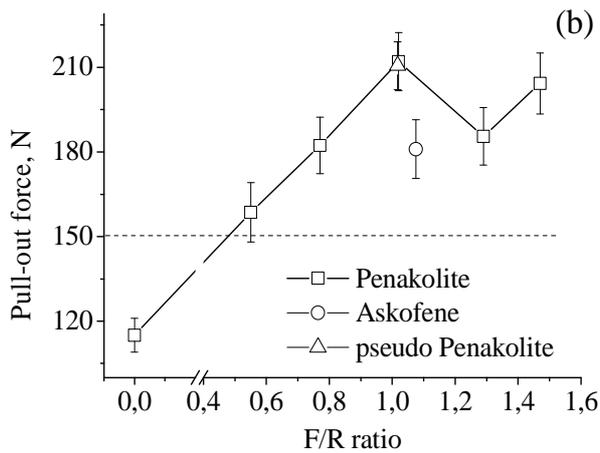


Fig. 1. a – Dependence of pull-out force on both polymer dispersion SB/AN ratio with CB (black square) or without CB (open squares); b – Dependence of pull-out force on formaldehyde-resorcinol (F/R) ratio in comparison with control sample (dashed line).

—□— dip with “prematured resin” Penakolite;  
 —○— dip with “prematured resin” Askofene;  
 —△— recalculated F/R ratio for the best recipe based on Penakolite using Askofene

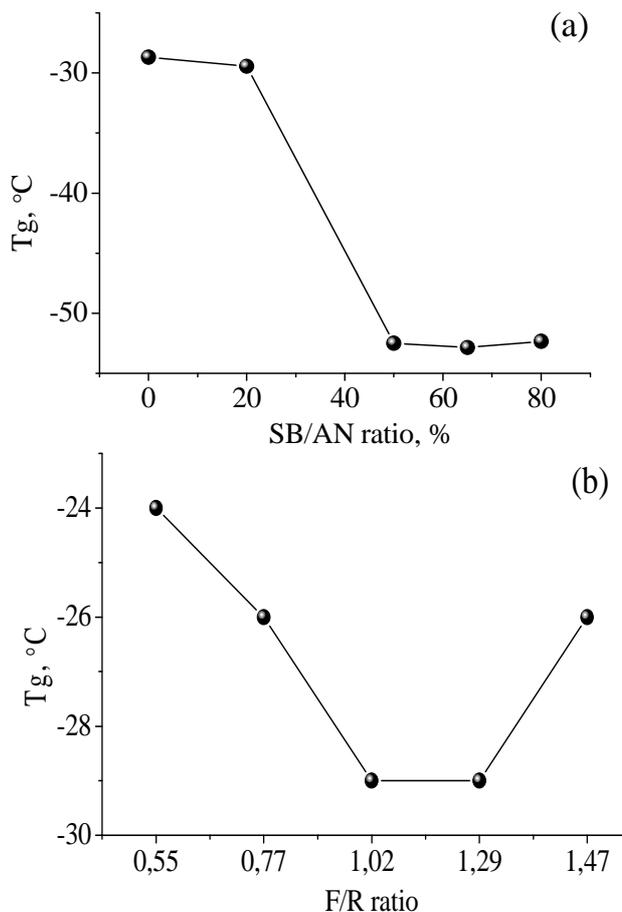


Fig. 2. Glass transition temperature dependence of a dip on SBR concentration (a) and F/R ratio (b)

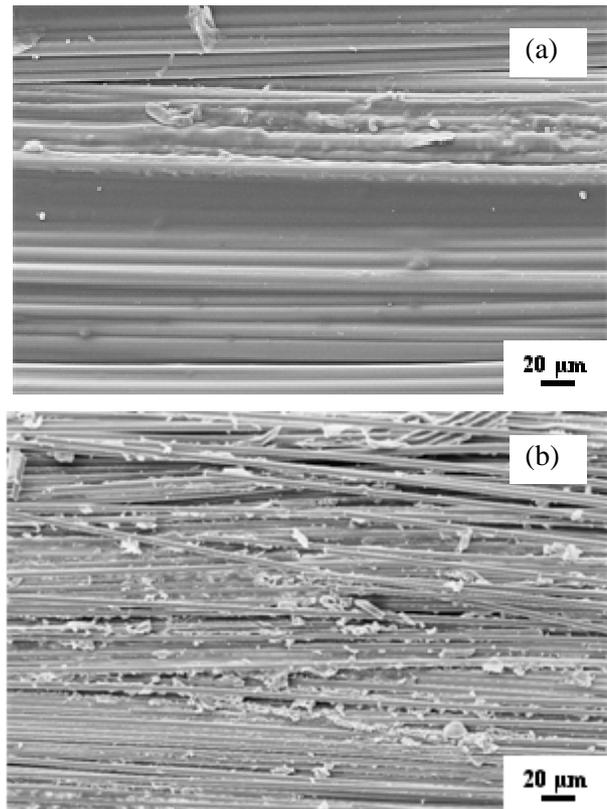


Fig. 3. SEM images of a dip surface before (a) and after (b) pull-out test.

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