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EFFICIENCY OF FULLY SCREEN PRINTED DYE SENSITIZED SOLAR CELLS WITH CONDUCTIVE POLYMER PEDOT:PSS COUNTER ELECTRODE

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Abstract

Dye sensitized solar cells (DSSC), the special group of photovoltaic cells, are standardly composed of TiO2 photoactive active electrode and counter electrode (CE) with catalytic platinum (Pt) layer on the glass substrate. However, the effort is put to the replacement of Pt with low cost conductive polymers which may be used and printed on flexible polymer foils instead of rigid glass substrate. The most widely used conductive polymer poly (3,4-ethylendioxythiofene) – poly (styrenesulphonate) (PEDOT:PSS) was used as a catalytic layer for DSSC counter electrode and screen printed on the glass substrate with fluorine doped tin oxide (FTO). Screen printed counter electrodes of PEDOT:PSS were compared to layers deposit with doctor blade technique. The results have shown that the DSSC based on counter electrode with double printed PEDOT:PSS layer reached promising 0.79 % and layer deposited with doctor blade reached 1.1 % efficiency compared to 1.09 % efficiency of DSSC with standard Pt counter electrode.

Introduction

Dye sensitized solar cells are possible replacement for conventional silicon based solar cells thanks to their promising photon to electron conversion efficiency, possibility to use low cost and environmentally friendly printing technologies (screen printing, roll-to-roll, doctor blade) and used materials (TiO2, carbon nanoparticles, conductive polymers). The DSSC standard structure contains five components, 1) glass substrate coated with transparent conductive oxides, 2) the semiconductor nonporous photoactive layer based on TiO2, 3) a dye used as sensitizer, 4) an electrolyte containing redox mediator, 5) and Pt counter electrode which has the crucial role in regenerating redox mediator and is responsible for the electron transport1.

The conductive polymer PEDOT:PSS is very well known for its high conductivity, good catalytic activity, high transparency, possibility to be used for different printing technologies and printed on flexible substrates. Due to these properties PEDOT:PSS is used and studied as a CE in DSSC. The DSSCs based only on one layer PEDOT:PSS counter electrode generate significantly lower efficiencies then those with Pt based CE2–5. Therefore, most researchers are focusing on the study of composites of PEDOT:PSS and carbon nanotubes which achieved 16 % lower efficiencies compared to Pt CE and about 30 % higher efficiencies compared to only one pure PEDOT:PSS counter electrode layer6. Disadvantages of composite materials based on PEDOT:PSS/CNTs are difficult and long homogenization process and a significant decline of CE transparency which decrease cell efficiency illuminated from the back – CE side.

The aim of this paper was to prepare fully printed dye sensitized solar cell with screen printed photoactive TiO2 electrode and polymer PEDOT:PSS multi-layered counter electrode. Properties as efficiency, transmittance of CE, volt-ampere characteristics and topography of DSSC using the counter electrodes with different numbers of screen printed or doctor bladed PEDOT:PSS layers on glass/FTO substrates were analyzed and compared with the standard DSSC containing Pt counter electrode.

Experimental

Preparation of nanoporous TiO2 photoactive anode

TiO2 paste for screen printing was prepared via homogenization process as mixture of 4.5 wt.% of TiO2 nanopowder (Evonik, Aeroxide P25, ~ 22 nm), 1,5 wt.% of ethyl cellulose (Aldrich, viscosity 22 cp in toluene:ethanol 80:20), 70 wt.% of ethanol (>96,6 %), 20 wt.% of deionized water and 4 wt.% of acetic acid (~99,7 %). The TiO2 nanopowder was added to mortar and stirred with gradual addition of acetic acid, deionized water and ethanol. The TiO2 dispersion was transferred with excess of ethanol and 10 wt. % of ethyl cellulose to a beaker and stirred with magnetic stirrer for 24 hours and then homogenized by ultrasonic bath for 20 min. The prepared TiO2 paste was screen printed (manual screen printer, polyester screen – 140 mesh, with mesh opening 64 μm, polyurethane squeegee and photosensitive emulsion Kasi, Fotocoat 1970), on the fluorine doped tin oxide coated glass (FTO glass, Aldrich, ~ 7 Ω/sq., 2×3 cm). After screen printing, the TiO2 electrodes with size 1×1,5 cm were sintered at 450–460 °C for 30 min to remove residual organic compounds and to improve interconnection between nanoparticles.

Preparation of PEDOT:PSS and Pt counter electrodes

Catalytic layer of PEDOT:PSS (Orgacon Type P 3042, transparent screen printing ink) with size 1x1.5 cm was screen printed (305 mesh, with mesh opening 34 μm) onto the FTO glass (2×3 cm). Samples with one, two and three printed PEDOT:PSS layers were prepared. Each layer was dried at 120 °C for 40 min before printing additional layer. Pt catalytic layer 1×1,5 cm (Solaronix, Platisol T/SP) was screen printed onto the FTO glass and then sintered at 450 °C for 15 min. On the case of doctor blade technique (DB), the FTO glasses with sticked scotch tapes (thickness 40 μm) on three sides were used. The movement of the blade created defined layer of 1×1.5 cm.

DSSC assembling

Prepared TiO2 photoactive electrodes were sensitized in 0.4 mM solution of N3 dye in ethanol (Aldrich, cis-[2,2’-binpyridyl]-4,4’-karboxyloxy-l2(NCS)3] ruténium(II)) for 24 hours. 18 μl of electrolyte (Solaronix, Iodolyte AN50) was added directly on the sensitized TiO2 electrodes which were then assembled with Pt or PEDOT:PSS counter electrodes.
into a sandwich type cell and caught with two binder clips. The photoactive TiO₂ layer has 1.5 cm².

DSSC and screen printed electrodes measurements

Transmittance of printed layers was measured with UV-Vis spectrophotometer Cecil CE 3055. 3D topography images, layer thickness and roughness were analyzed by atomic force microscope (Veeco microscope, 5 and 100 μm scanner, non-contact mode). I–V characteristic of DSSC were measured using day-light source with the power of 880 W/m² and by the loading circuit containing two multimeters (Keithley 2000).

Results and discussions

The thickness, roughness and topography of screen printed and DB coated PEDOT:PSS layers were evaluated by AFM. The single screen printed and DB coated PEDOT:PSS layer have similar thickness of 0.7 μm and 0.8 μm respectively. Double and triple screen printed layers have thickness of 1.4 and 2.1 μm. As shown in Fig. 1, the topography of DB coated layer was more flat with roughness Rq = 24 nm compared to screen printed layer with Rq = 28 nm. The roughness of screen printed layers decreased with the number of printed layers, for double printed layer to Rq = 23 nm and for triple printed layer to Rq = 21 nm. It indicates the filling of free spaces and the higher homogeneity of double and triple screen printed PEDOT:PSS layers.

The images of printed PEDOT:PSS layers taken from optical microscopy at 250× magnification (Fig. 2) shown that screen printed layers have surfaces marked by periodic structure of mesh fibers in positions where fibers cross each other. This inhomogeneity increased with number of printed layers.

Transmittance of printed CE layers, as an important factor for determination amount of accessible light to a dye, was evaluated at the wavelength of maximal absorbance of N3 dye λₘₐₓ = 534 nm. As shown in Fig. 3, highest transparency 75% at wavelength 534 nm was reached by FTO glasses with Pt catalytic layer, values for single screen printed PEDOT:PSS layer and PEDOT:PSS coated with doctor blade are very similar 70% and 69%. It is obvious that the increasing of number of screen printed PEDOT:PSS layers decreased CE transparency in whole UV-Vis spectrum.

The I–V characteristics of prepared DSSC were measured at front side (FS – the TiO₂ electrode) and back side (CE – the counter electrode) illumination. The Fig. 4 shows the I–V characteristics of prepared DSSC with screen printed and DB coated PEDOT:PSS counter electrodes measured from front side. The highest value of photocurrent density Jₘₚ = 2.59 mA cm⁻² (BS, Jₘₚ = 1.94 mA cm⁻²) reached CE with double screen printed PEDOT:PSS layers with the open circuit potential Vᵩₒᵩ = 0.68 V (BS, Vᵩₒᵩ = 0.67 V) with η =
coated PEDOT:PSS counter electrodes measured from front side Fig. 4.

0.64 %) followed single printed triple printed layer CE was reached by double printed layer 0.9 %. The highest efficiency of screen printed PEDOT:PSS CE and Pt CE with similar η = 1.1 % (BS, η = 0.79 % (BS, η = 0.9 %). The highest efficiency of screen printed PEDOT:PSS CE was reached by double printed layer η = 0.79 % (BS, η = 0.64 %) followed single printed η = 0.63 % (η = 1.1 %) and triple printed layer η = 0.53 % (η = 1.1 %).

Conclusions

The efficiencies of fully printed dye sensitized solar cells onto glass/FTO substrates with photoactive TiO2 electrode and conductive polymer PEDOT:PSS counter electrode were compared to standard DSSC based on Pt counter electrode. The DSSC with CE based on PEDOT:PSS double screen printed layers reached 0.79 % efficiency compared to η = 1.1 % doctor blade coated PEDOT:PSS layer and η = 1.09 % of screen printed Pt CE. The AFM and optical microscopy have shown that DB coated layers of PEDOT:PSS compared to screen printed have more flat surface without defects caused by screen printing mesh.

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0324-10, by the Slovak Grant Agency (project VEGA 1/0818/13) and by the OP Research and Development of the project National Centrum of Research and Application of Renewable Sources of Energy, ITMS 26240120016, co-financed by the Fund of European Regional Development.

REFERENCES


P-11
INFLUENCE OF FIBER PARAMETERS ON THERMOMECHANICAL AND MECHANICAL PROPERTIES OF MODIFIED PP FIBERS

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Introduction

High compressive strength, long service life, and low cost are properties insuring concrete to be the most commonly used construction material. Disadvantages of concrete as low tensile strength and crack resistance may be improved by reinforcing of concrete, what was investigated in numerous studies.

Fiber-reinforced concrete is concrete containing dispersed randomly oriented fibers. Fibers primarily control the propagation of cracks and limit the crack width. Concrete reinforced with short discontinuous fibers considerably improves the performance of concrete and negates its disadvantages such as poor toughness, a serious shortcoming of high strength concrete, low ductility, and low energy absorption capacity.

There are many kinds of metallic or polymeric fibers are used in concrete for their advantages. Polypropylene (PP) fibers are one of the most widely used for construction applications such as in shotcrete tunnel linings, blast resistant concrete, overlays, and pavements. PP fibers are commercially utilized at relatively low volume fractions to control plastic shrinkage cracking of concrete and they are expected to improve concrete ductility, toughness, and impact resistance.

However, addition of sufficient additive to PP fibers may provide further improvements in this field. Physical and chemical modification induces more intense adhesion of PP fibers to concrete matrix. Change of cross section of modified PP fibers from circle to star-shaped profile increases contact surface between fiber and concrete. This leads to expressive improve of functional of PP fibers in relation to transmission and absorption of deformation energy.

This article is focused on the structure and properties changes of polypropylene fibers after their modification by addition of inorganic filler with different cross section. Thermomechanical and mechanical properties of standard PP
fibers and PP fibers modified by inorganic additives with content 6.4 wt.% and 16.8 wt.%, with circle and star-shaped cross section were studied. Information about fiber structure was obtained from TMA scans. Tenacity at the break, Young’s module and elongation of PP fibers were obtained at determination of mechanical properties.

**Experimental**

**Material used**

In this study the specimens were prepared using PP TATREN HT 1810 with MFI = 20.6 g/10 min produced by Slovnaft a.s., Bratislava (SK). Using the two screw extruder has been PP and PP with different content of inorganic filler mechanically mixed and melted. Obtained concentrates have been subsequently used for preparation of fibers with circuit and star-shaped cross section by continual technology. Prepared PP standard fibers (PPS) and composite PP fibers with content of inorganic filler 6.4 %wt. (PPC1) and 16.8 %wt. (PPC2) has been drawn in the range of drawing ratios 2–4.

**Methods used**

The evaluation of thermomechanical properties has been performed using Shimadzu Thermomechanical Analyzer TMA–50. Temperature (T_D) at which the fibers are deformed at a constant load and shrinkage (l_D) of fiber at 90 °C were determined using the TMA scans showing shrinkage behavior before melting. Conditions of measurement were following: heat from room temperature to 90 °C at the heating rate 5 °C min⁻¹, and fiber length 9.8 mm.

Mechanical properties were measured by Instron 3343 device and evaluated using Instron program. Measuring conditions were: fixture length of fiber 125 mm, rate of clamp shifting 500 mm min⁻¹. Tensile test was done in order to measure the tension of fiber to tensile stress until the interruption of fiber. Fibers are straining continuously. Maximum tensile tenacity at the break and corresponding extension is measured at the rupture of fiber.

**Results and discussion**

Analysis of thermomechanical properties of PP fibers modified by various contents of inorganic additives was realized by TMA. Fiber prepared with both, circuit and star-shaped cross section, drawn to drawing ratio 2–4, were expose to temperature growth from room temperature to 90 °C at rate 5 °C min⁻¹. Obtained experimental dependencies are used for determination of dimensional stability of samples, specifically by deformation temperatures and total shrinkages. Dimensional stability depends on the orientation and crystallinity of the samples.

From results shown in Tabs I, II it is obvious that addition of inorganic additives does not lead to considerable decrease of deformation temperatures. PP fibers samples with circuit cross section actually indicate higher temperature resistance, which is growing with higher fiber orientation. Temperature growth with higher drawn ratio did not occur only at PPC samples with star-shaped cross section. Deformation temperatures of PP fibers with 6.4 wt.% content of inorganic additives reached highest values.

Measuring of dimensional stability of fibers proves shrinkage at all samples. In consequence of drawing samples the shrinkage grows, while addition of inorganic additive improves dimensional stability of PP fibers with circuit as

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well as with star-shaped cross section. In addition, fibers with circuit cross section achieved higher shrinkage than it was at PP fibers with star-shaped cross section, whereby differences decrease with increase of content of inorganic additives.

Evaluation of mechanical properties has shown dependency of tenacity at the brake of PP fibers on content of inorganic filler as well as on drawing ratio (Fig. 1). With increasing content of inorganic additives there is tenacity of PP fibers slightly lower, while orientation of fibers increases their tenacity. Tenacity at the brake of PP fibers with star-shaped cross section was lower at PP fibers with circuit cross section. Young’s module of star-shaped cross section of PP fibers was similar to fibers with circuit cross section. The highest values of Young’s module of modified PP fibers were measured at PPC1 fibers with star-shaped cross section.

Elongation (Fig. 2) decreases with fiber orientation. At PP fibers with circuit cross section there is observed increase of elongation at higher content of inorganic additives, while at PP fiber with star-shaped cross section there is higher elongation at 6.4 wt.% content of inorganic additives at lower drawing ratios.

Conclusions

Higher dimensional stability in dependence on temperature is achieved by PP fibers with 6.4 wt.% of inorganic additives, what is confirmed by higher deformation temperatures at PP fibers with circuit as well as with star-shaped cross section. PP fibers with star-shaped cross section have better dimensional stability at higher content of additives at circuit and star-shaped cross section. Dimensional stability increases with drawing ratio at all fibers as a result of higher input strain at fiber orientation. Modification of PP fibers with inorganic additives decreases their mechanical properties.

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REFERENCES


P-12
SOLID PARTICLES - THEIR EFFECT ON PROPERTIES OF COMPOSITE FIBRES

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Abstract

In this paper the effect of inorganic nano fillers, such as organoclay, boehmites and carbon nanotubes on spinning, drawing and mechanical properties of PP composite fibres was studied. The dependence between filler content, processing conditions and tensile properties of PP composite fibres are discussed.

Introduction

Oriented polymer nanocomposites such as nanocomposite fibres represent a special group of the polymer materials from the point of view of arrangement of nanofiller particles in polymer matrix.

Solid particles play an important role in modification the desirable properties of polymers. Compounding of polymers with suitable fillers is an effective way to improve the properties of composites, mainly mechanical, thermal, electrical as well as UV barrier and light stability.8

The montmorillonite (MMT) is one of the most commonly used organically layered silicates. Organically treated layered silicates are organoclays suitable for preparation of polymer nanocomposites with polar functional groups such as polyester (PES) and polyamide (PA). For polyolefin nanocomposites such as polypropylene (PP) and polyethylene (PE) it is necessary to use the convenient compatibiliser in addition.8

Boehmites are hydrophilic inorganic aluminium oxides based on γ-AIO(OH). With regard to hydrophilic nature the boehmites can be used also in latex and water solutions of polymers. After suitable surface treatment they are dispersible in the organic solvents and become interesting inorganic nano fillers for polymers10.

The carbon nanotubes (CNT) represent an unique nanofibrous materials for polymer composites because of their shape, morphology, electrical and mechanical properties. The high variability in morphology of CNT as well as the lack of precise knowledge regarding to structure and properties of CNT prevent their more widely application in thermoplastic composites. The chemical modification e.g. surface functionalization of CNT and suitable compatibiliser may improve their disintegration and distribution in polymer11.
Experimental part

Polymers: Polypropylene (PP): PP HF 500R, MFR 25 g/10 min, flakes; PP Moplen HP561N, MFR 11 g/10 min, and PP Moplen HP561R, MFI 25 g/10 min.
Fillers: Disperal 40 (D40), Disperal 60 (D60), Disperal modified with undecylenic acid (DUN) and Disperal modified by 3-aminopropyltriethoxiloxane (DAM).
Cloisite 15A (C15A), and Cloisite 30B (C30B), Multi-Wall Carbon Nanotubes – Nanocyl® 7000 (CNT).
Compatibilisers: Slovacid 44P and Tegopren 6875.

Preparation of PP composite fibres

The conventional concentrate technology was used for preparation of PP nanocomposite fibres. The method consists of two steps: preparation of PP/filler concentrate dispersions using the twin-screw extruder (d=28 mm) and spinning of mixture of the PP and PP concentrate dispersions to obtain the final concentration of filler in the fibres.

Method used

The Instron (Type 3343) was used for the measurements of the mechanical properties of fibres (according to ISO 2062:1993). Coefficients of variation of tensile strength and elongation at break were used as measure of internal (structural) non-uniformity of fibres.

Results and discussion

The effect of solid particles on parameters of the supermolecular structure of both spun and drawn fibres is very important for assessment of processing of polymer composite in spinning and drawing at conventional sinning speed. Especially, inconvenient supermolecular structure of PP spun fibres and non-uniform distribution of solid particles can negatively affect the drawing process and mechanical properties of fibres.

The results on the Fig. 1 reveal the effect of filler content on mechanical properties of PP composite fibres. The results obtained indicate that the tenacity of the fibres increase with content of nanofillers pass through maximum and above 0.3 wt.% decrease gradually with higher concentration of nanofillers. Maximum tenacity and modulus of the PP composite fibres were obtained at low concentration up to 0.2 wt.% for all kinds of Disperals and Cloisites.

Tenacity and Young’s modulus of PP/MWCNT composite fibres decrease gradually with content of the fibrous particles in PP fibres. The tensile strength of fibres unambiguously decreased for fibres containing more than 0.1 wt.% of MWCNT (Fig. 2). The low elongation at break and high non-uniformity of the mechanical properties are characteristic for the fibres with content of MWCNT higher then 0.1 wt.%.

Higher concentration of MWCNT affects negatively processing of composites at spinning and drawing. Therefore, the combination of MWCNT with other additives such as organoclayes, boehmites, and compatibilisers-dispersants based on derivatives of polyglycols and polysiloxanes, was used to obtain required processing, structure and properties of fibres.

Analysis of these results leads to conclusions that higher mechanical properties including positive effect of nanofillers in PP matrix can be obtained only at optimized composition of the composites and spinning as well as drawing conditions.

Conclusions

The results show that the processing of the PP composites strongly dependences on concentration of solid particles (fillers) and spinning conditions. Spinnability
dies with content of the fillers in PP matrix. The effect of spinning temperature, take-up velocity as well as drawing temperature is very important and influences the structure and mechanical properties of final PP composite fibres.

The tenacity and Young modulus of PP composite fibres containing up to 1.0 wt.% of solid particles (boehmite, CNT) were significantly increased (up to 20 %) in comparison with PP standard fibres. Some selected compatibilisers also contribute to mechanical properties of composite fibres.

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REFERENCES


P-13

INFLUENCE OF FLAME-RETDARTANTS ON MECHANICAL PROPERTIES AND THERMAL STABILITY OF EPOXY RESIN COATINGS

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Abstract

The modified epoxy resin coating were prepared by adding flame-retardant to commercial epoxy prime coat. The aluminum trihydroxide (ATH), nano size magnesium hydroxide (MH) and aluminum-layered double hydroxides (LDH) have been used as flame-retardants. The mechanical and thermal properties of the epoxy coating have been investigated. The aim of this paper has been determined by the optimal content of flame-retardant in coating compositions based on epoxy resin.

<table>
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<th>Content wt.%</th>
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<tr>
<td>0</td>
<td>C ATH C5ATH C10ATH C15ATH C20ATH C25ATH C30ATH</td>
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<td>5</td>
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Introduction

The fire protection of metallic elements with use of polymer materials have become an important issue in the automotive, construction and marine industry. The coating systems have been applied to improve the appearance, adhesion, toughness, corrosion resistance and durability of products. Epoxy resins have good mechanical properties, chemical resistance as well as low shrinkage on cure and superior adhesion to many substrate. Nevertheless, the main problem during epoxy resins processing is their flammability. Materials coated by systems based on epoxy resins with flame retardants have gained fire penetration and flame spread resistance. The recent investigation into the application of nano-size flame retardants to coating has indicated that nano-fillers can improve both the physical and chemical properties of polymer materials. Interesting are also the layer double hydroxides LDH which are inorganic materials made of magnesium and aluminum nanoparticles. However, significant improvement of fire resistance efficiency in LDH composites depends on homogeneous dispersion of nanofillers in the polymer matrix. The widely used flame retardants are magnesium hydroxide (MH) and aluminum trihydrate (ATH), which are economic, but their efficiency requires higher content than nano fillers.

In this paper the optimal content of flame-retardant in epoxy composition as well as mechanical properties of the coating have been investigated. The aluminum trihydroxide (ATH), nano size magnesium hydroxide (MH) and aluminum magnesium layered double hydroxides (LDH) were used as flame-retardants.

Experimental

The studied formulation was the commercial epoxy prime coat PROTECT 360 (Industrial coating system Novol) cured with hardener H 5960 (Novol). Aluminum hydroxide (Sigma-Aldrich), nano-Magnesium hydroxide (nanopowder, <100 nm Sigma-Aldrich), aluminum magnesium layered double hydroxides (Perkalite LD, Akzo Nobel) were used as flame-retardants. The epoxy prime coat, flame-retardants and hardener were mixed together using a mechanical stirrer. The weight ratio of epoxy to hardener was 4:1. The amounts of flame-retardants used in this study range from 5 to 30 weight percentage. The names of samples are listed in Table I. The
final compositions were spread to steel plates with a low pressure HVLP spray gun (diameter of nozzle 1.7). The average layer thickness was 80 µm. Samples were cured at ambient temperature during 24 h.

Test methods

The investigation of the coatings impact resistance was carried out in accordance with PN EN ISO 6272/1 i.e one kilo spherical indenter was dropped down onto the coated sample. The drop height was adjusted to 25–100 cm to achieve property impact energy. The cross-cut adhesion tests of the coating samples were carried out as per ISO 2409. The six lines on the coatings were cut with a cutting blade. Then a cutting tool was rotated by 90° and next six lines were mark through the coating. The adherence of the coating was determined by using adhesive tape\textsuperscript{[10]}. The thermal property of the coatings was determined by thermogravimetric analyses (TGA) with a temperature range between 30 and 900 °C at a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere using a TG 209 F1 Netzsch. About 10 mg of powder was taken from the steel plates’ coating for measurement. The initial decomposition temperature Ti was determined as the temperature at which the weight loss was 5%. The residual mass ($\Delta W\%$) was defined at 900 °C.

Results and discussion

The results of the mechanical tests of epoxy coating are presented in Table II. The effects of impact tests indicated better performance of the modified coating compared with the commercial epoxy prime coat-C. For samples C10MH, C15ATH, C15LDH, C20LDH, C25LDH, C30LDH a 95 cm drop heights and for samples C and C5MH 80 cm drop heights were observed.

All the coating compositions filled with LDH as well as four types of samples with ATH show the highest cross-cut adhesion value (0°; Table II). These types of coatings exhibit good properties during the adhesion tests, smoothness of the cut edges as well as no detachment of any layer parts. On the contrary, compositions filled with MH and commercial compositions exhibit worse adhesive properties (Fig. 1).

The differences observed in mechanical properties of the samples are most likely influenced by different dispersions and characteristics of metal hydroxides particles.

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<td>C10LDH</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>C15LDH</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>C20LDH</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>C25LDH</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>C30LDH</td>
<td>95</td>
<td>0</td>
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</table>

Thermal stability of epoxy coating is presented in Table III. The Ti of commercial compositions was 337.2 °C. Nevertheless, the modified coating has indicated lower values of thermal stability. The samples with MH began to decompose at 333–334 °C. The Ti of coating with ATH and LDH decrease slightly with a growing flame retardant content. The difference in degradation behavior of these epoxy coatings took place probably due to the fact that ATH, MH and LDH have begun to decompose at lower temperatures than components of commercial epoxy coat. For

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Ti [°C]</th>
<th>$\Delta W%$, 900 °C</th>
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</thead>
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<tr>
<td>C</td>
<td>337.2</td>
<td>56.87</td>
</tr>
<tr>
<td>C5MH</td>
<td>334.6</td>
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<tr>
<td>C10MH</td>
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<tr>
<td>C30LDH</td>
<td>301.0</td>
<td>56.76</td>
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</table>
all composites coatings the residual mass of was about 56 to 60%.

The thermal stability gives indirect information about the potential flame retardancy of the polymer modified materials. The mechanisms of flame retardancy will vary depending on the used flame retardant type. The metal hydroxides absorb the heat during fire and send out \( \text{H}_2\text{O}, \text{CO}_2 \) which lowers temperature of polymeric materials. The initial decomposition temperature indicates the thermal stability of the epoxy coating, i.e., the failure temperatures of the resins in processing and moulding.

Conclusion

The aluminum trihydroxide (ATH), nano size magnesium hydroxide (MH) and aluminum magnesium layered double hydroxides (LDH) was introduced into the commercial epoxy prime coat. It have been found that the modified coatings have better mechanical and adhesion properties than the commercial epoxy prime coat. The thermal gravimetric analyses have indicated that flame retardants decrease the thermal stability of the coating, thus it is difficult to determine the optimal content of flame retardant in coating compositions. Besides, the application of the flame retardants, for commercial epoxy prime coat is not recommended in case of thin layer coatings.

The authors would like to thank NOVOL Sp. z o.o for their help and support.

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weight ratios of PP/PS were equal to 100/0, 75/25, 50/50, 25/75 and 0/100. This mixing process was repeated five times.

After each recycling process a part of every material was injected on the injection molding machine (Battenfeld Plus 35/75). As a result the samples required for further tests on mechanical properties (type 1A according to PN-EN ISO 527-2, ref.7) were produced.

**Methods**

In order to execute the mechanical tests a Zwick Roell Z020 testing machine, conjugated with a computer, and with a tensile strength measurement head in the range between 0–20 kN was used. For all the samples tensile and flexural strengths were determined and for all types of recycled materials this test was repeated five times.

For hardness determination the Brinell hardness tester (KB Prüftechnik GmbH, KB150R model) was used. Each sample was subjected to deformation during the time of 30 s with different loads – 132 N for polypropylene and polymer blends, and 358 N for polystyrene.

The temperature during all measurements was 21°C.

**Results and discussion**

Strength tests provide valuable information about the mechanical properties of the tested materials and determine potential applications for the finished product. Obtained results for recycled body kits from polypropylene, polystyrene and their blends are presented in Fig. 1–3.

The reported values of Young’s modulus (E) as a function of the processing times and the composition of polymer blends are presented in Fig. 1. After analyzing the test results, it is clear that the properties of the polymer mixture are similar to the properties of the polymer, which forms the continuous phase of the mixture.

Considering the processing times it was noted that in case of polypropylene and a blend containing 25 wt.% of polystyrene the Young’s modulus increases with the processing times up until the third cycle and then becomes constant. This suggests that in case of these materials three-times reprocessing causes the improvement of the mixture’s homogeneity. In case of PP/PS blends with a weight ratio equal to 50/50 and 25/75 and polystyrene, the determined modulus of elasticity was at a constant level (within the limits of statistical error for consecutive measurements). Obtained results confirmed the rightness for common mechanical recycling of car spoilers made of PP and PS. The fact worth emphasizing was that similar dependence was also obtained for the designated true tensile stress and elongation at break.

The above conclusions also confirmed the results of flexural tests, as shown in Fig. 2. After analyzing the results it can be stated that with the increasing re-processing times the flexural modulus (E_f) in bending for polystyrene does not change – five times processing does not deteriorate PS stiffness. It was observed that in case of polypropylene, up until the second recycling time, the flexural modulus increased from 1.42 GPa (0x) to 1.55 GPa (2x) and then begun to decrease. However, the fifth processing does not result in lower rigidity in comparison to the input material. In case of PP/PS mixture (50/50) the value of the modulus oscillated at 1.85 GPa. The same was observed for PP/PS (25/75) where the value was 2.40 GPa. Significant differences were noted only for PP/PS (75/25) – the value of the second reprocessing was maintained at a constant level and then started to decrease rapidly.

![Fig. 1. Young’s modulus as a function of multiprocesing and the PP/PS weight ratio](image1)

![Fig. 2. Flexual modulus as a function of multiprocesing and the PP/PS weight ratio](image2)

![Fig. 3. Brinell hardness as a function of multiprocesing and the PP/PS weight ratio](image3)
The results of hardness tests (HK) are presented in Fig. 3. After analyzing the mechanical properties resulting from static stretching and bending, it might be assumed that the hardness of the mixture will increase with an increasing amount of polystyrene in the mixture. In Fig. 3 it can be seen that in case of five-times processing of polypropylene and all of polypropylene/polystyrene blends similar hardness values are observed. They begin to stabilize at the same level. The hardness of polystyrene revealed a growing trend in multiple processing.

**Conclusion**

Summarizing the results of the research it was found that the mechanical recycling of mixed (immiscible) plastic materials (like a PP and PS) is justified. The mechanical properties of input materials (PP, PS) and their blends expectancy are changed as a function of the composition structure – all mechanical properties of PP/PS blends are mainly determined by the material forming the continuous phase of the mixture (the phase inversion phenomenon).

Moreover, it was found that multiprocessing (five times) of polymer blends (PP/PS) (non-separated processing) has an insignificant influence on mechanical properties of recycled products. Polymer blends produced from re-granulate have good tensile strength, flexural and hardness, so they can be successfully used in many industries as well as in automotive.

This work was supported by grant 32-379/2013 DS-PB.

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7. PN-EN ISO 527-2. Tworzywa sztuczne: Oznaczenie właściwości mechanicznych przy statycznym rozciąganiu
Experimental

Materials

Poly(vinyl alcohol) Poval 205 (degree of hydrolysis 88 %, Kuraray Japan), glycidylmethacrylate (GMA; Merck), maleic anhydride (MA; Aldrich), dimethylaminopyridine (DMAP, Aldrich), N,N-dimethylformamid (DMFA, Lachema, Czech Republic), dimethyl sulfoxide (DMSO, Merck), ethanol (Merck), acetone (Merck) and Irgacure®2959 (Ciba, Switzerland) were used as received.

Preparation of poly(vinyl alcohol) derivatives

In this work two types of poly(vinyl alcohol) derivatives containing polymerisable groups (MA PVA, GMA PVA) were synthesized.

Preparation of MA PVA and MA PVA 1 (PVA modified by maleic anhydride): 8.8 g PVA was dissolved in 50 ml water and 50 ml DMFA at 90–100 °C. After dissolution of PVA, the temperature was dropped to 60 °C and 9.3 g of maleic anhydride was added and let to dissolve. After its dissolution, 0.098 g of the catalyst (DMAP) was added, but only at the preparation of MA PVA 1. After 5 hours the mixture was let to cool down to room temperature, then precipitated in acetone and washed twice with ethanol and acetone. Washed product was dried at 37 °C till constant weight and ground into fine yellow powder.

Preparation of GMA PVA (PVA modified by glycidyl methacrylate): 10 g PVA was dissolved in 50 ml DMFA and 25 ml DMSO at 90 °C. After complete dissolution, the mixture was cooled down to 70 °C and 2.5 ml of GMA and 5 ml of 5 wt.% ethanolic solution of KOH was added dropwise. Mixture was kept at 70 °C for one hour and constantly agitated. Then it was cooled to ambient temperature, diluted with 25 ml of water and the product was precipitated into an excess of acetone. The precipitate (GMA PVA) was collected, washed in acetone and dried to constant weight at room temperature.

Preparation of samples and UV curing of coatings

The samples were prepared by mixing the aqueous solution of modified PVA (MA PVA, MA PVA 1 and GMA PVA) with photoinitiator Irgacure®2959 (3 wt.%). These compositions coated on the aluminum plates were irradiated by a medium pressure mercury lamp 250W (RVC, Czech Republic). The curing process was evaluated by IR spectroscopy (FTIR spectrophotometer EXCALIBUR SERIES Digilab FT3000 NX, USA).

The degree of conversion in the cured film was determined according to the amount of double bond (twisting vibration at 810 cm⁻¹, stretching vibration at 1610–1640 cm⁻¹) by a baseline method. The degree of conversion X was calculated from well-known equations:

\[ X = 1 - \frac{[A]_0}{[A]_t} \]  

(1)

where \([A]_0\) and \([A]_t\) is the absorbance measured at the chosen wavelength before and after the exposure to UV light for the time \(t\), respectively. The values of maximum conversion \(X_{\text{max}}\) were obtained from the plots of \(X\) vs. time.

Results

The hydroxyl groups of the PVA were esterified by introduction of groups with unsaturated photochemically active bond. In order to prepare the modified poly(vinyl alcohol) with defined concentration of ester groups, we optimized the preparation of maleinated PVA (MA PVA). For derivatives preparation we used various amount of maleic anhydride, to some samples we added catalyst (pyridine, DMAP, p-toluensulfonic acid) and we changed the esterification time too. The conversion degree, i.e. extent of modification expressed as a molar fraction of modified monomeric units of the PVA macromolecular backbone, was quantified by acidobasic titration. In this work we used two prepared derivatives of PVA achieved at modification described in experimental part: MA PVA (without catalyst, esterification time 5 h, esterification degree 10 %) and MA PVA 1 (1 %wt. DMAP according to the mass malein anhydride, esterification time 5 h, esterification degree 16 %).

FTIR spectroscopy was used to examine the modification and structural changes between original PVA and prepared modified PVA. By comparing of the spectra in Fig. 1, we observed that new peaks at 1638 and 815 cm⁻¹ have emerged. These are due to C=O stretching and twisting vibrations. We also observed the extension of C=O peak at 1730 cm⁻¹, what confirms the inclusion of ester group into the molecule of PVA.

GMA PVA was prepared according to recipe described in experimental part. The modification reaction performed on PVA lead to the epoxide ring opening and the attachment of hydroxypropyl methacrylate moieties onto the PVA macromolecular backbone. The successfulness of modification was confirmed by FTIR spectroscopy (Fig. 2),

Fig. 1. FTIR spectra of poly(vinyl alcohol) POVAL 205 (full line), modified poly(vinyl alcohol) MA PVA 1 (dash line). Inset FTIR spectrum of maleic anhydride
new peaks at 1634 and 810 cm\(^{-1}\) and the shift of peak at 1730 cm\(^{-1}\) were observed, peak at 1660 cm\(^{-1}\) has disappeared.

The UV curing process will be performed through radical polymerization of unsaturated groups in the lateral moieties. For the preparation of photochemically cured compositions a photoinitiator Irgacure®2959 ([4-(2-hydroxyethoxy) phenyl-(2-propyl) ketone]) was added to both prepared PVA derivates. It is a radical photoinitiator of 1\(^{\text{st}}\) type, where radicals are created due to cleavage Norrish I (ref.\(^{8}\)). The exposure by medium pressure mercury lamp caused the photopolymerisation, which shows as a decrease in the absorbance bands in the C = C bond in the FTIR spectrum. We observed spectrum decrease in range of 1630–1640 cm\(^{-1}\) and the change of conversion depending on exposition dose (exposition dose = light intensity x time). The absorbance was recalculated by the equation (\(I\)) to the conversion. The curing occurred at the intensity of incident light 12 mW cm\(^{-2}\). The maximal conversion degree was reached at the initiator concentration of 3 wt.% (Fig. 3). Probably the higher initiator concentration exhibits high absorption at its absorptions maximum at 280 nm, and the initiator acts as internal filter. The maximal conversion degree reached at exposition dosage 29 mW cm\(^{-1}\) was 65 % for MA PVA and 70 % for GMA PVA. The both compositions were good cured. For composition with MA PVA (prepared without catalyst) the maximal conversion was only 38 %. The composition was uncured in fact and tacky. However, in the case of MA PVA sufficient conversion can not be reached even after substantial extension of curing time.

Conclusions

Two types of modified photopolymerizable derivatives of PVA (MA PVA, GMA PVA) were synthesized. Reaction conditions were optimized in order to obtain such extend of modification (i.e. conversion degree) which would ensure efficient crosslinking.

The UV curable polymer films were prepared by addition of radical type photoinitiator Irgacure®2959 (1 wt.%), which would be to both modified PVA. According to spectroscopic monitoring of the curing process we can say, that the curing was more effective for PVA GMA (higher conversion of double bond was reached).

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