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Pigment and Dye Modified Fillers as Elastomeric Additives

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1. Introduction

Pigments are a dynamically developing area of chemical technology. This interesting scientific concept involves preparation of hybrid pigments by the formation of a stable dye sphere surrounding an inorganic substrate grain, such as silica, titanium dioxide, or aluminosilicates. The concept of combining properties of organic and inorganic pigments has been employed for a long time. At the end of the 19th century, this concept was applied to the production of a pigment lake where freshly precipitated aluminium hydroxide was employed as the support. These lakes were used for the production of graphic dyes due to their averaged properties. Silica, zinc oxide, carbon black, and titanium dioxide may be employed in rubber compounds as pigments and fillers. Fillers boast a wide range of industrial applications, such as in the pharmaceutical and textile industries, and are important as additives for paints and varnishes. Fillers are relatively inexpensive, solid substances that are added in fairly large volumes to polymers to adjust the volume, weight, cost, surface, colour, expansion coefficient, conductivity, permeability, and mechanical properties. They can be roughly divided into inactive or extender fillers and active or functional or reinforcing fillers. One of the most popular fillers is synthetic silica, which is used in the polymer industry as an active filler (Liu et al., 2008, Wang et al., 2009). The rubber industry utilises fine silicas, which have a large specific surface leading to favourable effects on the strength of the composites. One important processing challenge is that silica surfaces are hydrophilic in nature, which impedes their dispergation in polymer media. Nearly all of the silica forms tend to agglomerate, which is an undesirable behaviour from the point of view of utilising their functional properties in industrial applications. On-going research on this topic focuses on altering the characteristics of the filler surfaces through some type of modification (Ciesielczyk et al., 2007; Ciesielczyk et al., 2011; Klapiszewska et al., 2003; Kohno et al., 2011; Ladewig et al., 2012; Kishore et al., 2012; Natinee et al., 2011). For example, industry has developed hydrophobic silicas that easily dispergate in polymers. The

production of these silicas involves a silica silanisation reaction with alkoxysilane containing functional groups (Jesionowski et al., 2001; Kryszewski et al., 2000; Elham et al., 2012; Kister et al., 2012; Jianzhong et al., 2011; Wunpen et al., 2011; Jung-Woo et al., 2011). Over the past decade, numerous studies have employed a dye to modify the surface of silica to obtain hydrophobic silica surfaces and visually appealing end product colours (Ansarifar et al., 2004; Al Dwayya et al., 2012). The presence of amino groups in these supports enables the formation of ionic bonds with acid and direct dyes as well as the formation of covalent bonds with reactive dyes (Donia et al., 2009). Dyes, which were applied for this purpose, belonged to the textile class. Although they were combined with silica, they could not fulfill the requirements of modern pigments, such as light-resistance or resistance to solvents and to high temperature. High temperature during polymer processing can damage or destroy the dye causing changes in the shade or loss of colour. The present study was directed at obtaining composite pigments of indigothiazine and silicas with different surface areas. Indigothiazine consists of two thiazine residues conjugated to each other by a double bond. Because their cyclic carbonamide groups, thiazine can form hydrogen bond to silanol groups present on the silica surface. The thiazine pigments exhibited good heat stability, insolubility and exposure durability. An alternative method of producing coloured fillers is via a mechanical approach in which a coloured organic system is mechanically applied to the surface of a non-organic support. This method is a simple and cheap method of producing an organic-inorganic pigment encasing silica in the coloured chromophore with the additional benefit of eliminating the undesirable solvents from the process. The anti-ageing properties of indigothiazine were confirmed by oxidation-reduction potential measurements. The composites were produced by mechanically applying a coloured organic system (indigothiazine pigment) to a non-organic support (silica). The prepared pigment composites were characterised by the following properties: agglomerate size distribution, zeta potential, and specific surface area of the silica fillers before and after application of indigothiazine. The composite pigments were evaluated for their functional properties and subsequently employed as fillers in an acrylonitrile butadiene rubber (NBR). The mechanical properties as well as the spectrophotometric and DSC data of the vulcanisates produced with the composite pigment fillers were also studied before and after being aged under UV radiation.

2. Colourants in polymer composites

2.1. Fillers modification

Compared to inorganic pigments, organic pigments exhibit greater vividness, higher colour intensity and higher staining potential. Their drawbacks include greater sensitivity to the action of chemical compounds, temperature and solvents (Binkowski et al., 2000). Several studies were conducted to obtain organic pigments that were permanently attached to a silica core to improve the resistance of the pigments to chemical and thermal treatments. Numerous studies have shown that the reaction mechanism that occurs on the surface of inorganic substances is extremely difficult to identify. For example, the reaction that occurs on the surface of silica with fluorescein results in the formation of covalent bonds between

the reagents. The interactions may involve the formation of hydrogen bonds as well as van der Waals or electrostatic interactions (Jesionowski 2003; Wu et al., 1997). Silica is one of the most popular fillers employed as a pigment carrier. Silicas are extensively modifiable materials. Their modification results in products that have new functional groups on their surface and are capable of interacting with various organic compounds. For example, modification with aminosilane provided functional amino groups that can react with the carbonyl groups of aldehydes, ketones or esters. The aminosilane-modified silicas find multiple applications as polymer fillers in industry. Recently, they have been used with increasing frequency as coupling agents in pigment or organic systems. Until recently, studies of organic pigments involved modification of their basic properties, such as stability or intensity of the colours. However, in many cases, the pigments must satisfy additional requirements (e.g., well defined particle diameters). Pigments with silica cores can satisfy these requirements (Krysztalkiewicz et al., 2003). Bińkowski (Bińkowski et al., 2000) proposed a simple procedure for obtaining coloured silicas, which involves attaching the dye to a modified silica surface. The procedure is possible due to the availability of a wide range of commercial dyes. The resulting pigment exhibits a structure in which the silanol groups on the surface of the silica are chemically coupled to an organic dye (e.g., azo dye) through an aminosilane coupling agent. They represented the pigment structure using the following formula: $S-(O-Si-R^1-Z-D)_n$ where R^1 is the alkyl group, Z is the amine bridge fragment, D is the dye, n is a number not less than 1 and $-Si-R^1-Z-$ represents a group originating from the silane coupling agent. In this work, they employed precipitated silica, 3-aminopropyltriethoxysilane (U-13), 2-(aminoethyl)-3-aminopropyltriethoxysilane (U-15) and a dye obtained from Boruta-Kolor, C.I. Direct Red 81. The modifications resulted in uniform pigments. A subsequent report by the authors (Jesionowski et al., 2011) showed the adsorption of C.I. Mordant Red 3 on the surface of silica that was both unmodified and modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane. They proposed two mechanisms for the dye addition to the silane modified silica surface including via a hydrogen bond between the hydroxyl group of C.I. Mordant Red 3 and the amine groups of the silane coupling agents and/or via electrostatic interaction between the dissociated anion of the dye and the cation appearing on the silica surface modified with silane. Sudam (Sudam et al., 2003) described the adsorption behaviour of selected styryl pyridinium dyes on silica gel. The adsorbents were styryl pyridinium dyes with a monochromatic group containing an alkyl chain at the pyridinium nitrogen and a bichromatic group containing methylene groups bridging at the pyridinium nitrogen atoms. They observed that the bichromophoric dyes anchor on the silica surface in a flat-on position in which the methylene units also come in contact with the silica surface. Andrzejewska (Andrzejewska et al., 2004) performed studies to obtain pigments by adsorption of organic dyes on the modified surface of a titanium dioxide pigment system. The titanium oxide surface was modified with silane coupling agents, such as 3-aminopropyltriethoxysilane (U-13), *N*-2-(aminoethyl)-3-aminopropyltriethoxysilane (U-15D), in various solvents (methanol, toluene, acetone and methanol-water mixture). C.I. Acid Orange 7 and C.I. Reactive Blue 19 were employed to prepare the pigments. The organic dyes were deposited on the surface of the modified titanium white. The modification of the titanium white with both silanes (U-13 and U-15D) boosted the efficiency of adsorption of C.I. Acid Orange 7 dye on the surface. The improved adsorption efficiency of C.I. Reactive Blue 19 on the titanium was obtained

following modification with silane U-13. For the titanium modified with U-15D, the efficiency of C.I. Reactive Blue 19 dye adsorption decreased slightly. A subsequent report (Raha et al., 2012) proposed a new type of inorganic carrier, Na-montmorillonite (MMT). If the carrier is a smectite clay or layered silicate, the most effective pathway found involved using the ion exchange process. For that reaction, the dye must exist in a cationic form, which is the case for basic or cationic dyes. Example for that intercalated products of Rhodamine dyes with hectorite, montmorillonite and other smectite silicates. The synthesis of the water-soluble cationic dyes was performed using two azo dyes (i.e., Solvent Red 24 and Solvent Yellow 14) and one disperse dye (i.e., Red 60) intercalated with Na⁺-MMT to create nano-structured pigments. The dye-intercalated montmorillonite was successfully obtained. The modification of the dyes into their respective cationic species was confirmed by NMR study, and XRD indicated that these nanopigments had a nanostructured morphology. The authors also observed that the use of the nanopigments in PP reduced the migration of the dye, which results from the intercalation /adsorption of the dye within the clay-based pigments. The most common methods of modifications are presented in Table 1.

Type of supporter	The type of coupling agent	Type of dye	Reference
Silica	-	D&C Red 6, Acid Yellow 1, Acid Blue 25, Guinea Green B	Wu et al., 1997
Silica	-	Monochromatic and bischromatic styryl pyridinium dyes	Parida et al., 1997
Silica	3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropyltriethoxysilane	C.I. Direct Red 81	Binkowski et al., 2000
Sodium-aluminium silicate	Vinyltris(β-methoxyethoxy)silane; γ-methacryloxypropyltrimethoxysilane	-	Werner et al., 2001
Silica	N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Reactive Blue 19	Jesionowski et al., 2002
Silica	N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Reactive Blue 19, C.I. Acid Red 18	Jesionowski 2003
Silica	N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Acid Red 18	Jesionowski et al., 2003
Silica	3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropyltriethoxysilane, 3-ureidopropyltriethoxysilane	C.I. Acid Red 18, C.I. Acid Violet 1	Krysztalkiewicz et al., 2003
Silica	N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Reactive Blue 19, C.I. Acid Green 16, C.I. Acid red 18, C.I. Acid Violet 1, C.I. Direct Red 81	Jesionowski et al., 2004
Titanium dioxide	3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Acid Orange 7, C.I. Reactive Blue 19	Andrzejewska et al., 2004

Type of supporter	The type of coupling agent	Type of dye	Reference
Silica	<i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Basic Blue 9, C.I. Basic Blue 9, C.I. Acid Orange 52	Jesionowski et al., 2005
Magnesium silicates	<i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane; octyltrimethoxysilane; 3-chloropropyltrimethoxysilane; vinyltrimethoxysilane	-	Ciesielczyk et al., 2007
Montmorillonite	-	Thioindigo	Ramirez et al., 2011
Magnesium silicate	<i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane; 3-glycidoxypropyltrimethoxysilane	C.I. Basic Blue 9, C.I. Acid Yellow 17	Ciesielczyk et al., 2011
Silica	Imidazolium ionic liquids	Indigothiazine	Marzec et al., 2010
Silica	Imidazolium ionic liquids	Berberine chloride; 2-hydroxy naphthol quinone	Marzec et al., 2011
Silica	<i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Mordant Red 11	Jesionowski et al., 2011
Silica	<i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	C.I. Mordant Red 3	Jesionowski et al., 2011
Na-Montmorillonite	-	Solvent Yellow 14, Solvent Red 24, Disperse Red 60	Raha et al., 2012
Silica	3-aminopropyl trimethoxysilane	C.I. Acid Blue 113, C.I. Acid Red 114, C.I. Acid Green 28, C.I. Acid Yellow 127, C.I. Acid Orange 67	Aniba et al., 2012

Table 1. Common methods for the preparation of pigments.

2.2. Organic and inorganic pigments

Colourants used in polymers are pigments or dyes (Drobny, 2007). Dyes are organic compounds that are soluble in the polymers forming a molecular solution. They produce bright, intense colours and are transparent and easy to disperse and process. In general, pigments are insoluble in polymers. They produce opacity or translucence in the final product. Pigments can be inorganic or organic compounds and are available in a variety of forms, such as dry powders, colour concentrates and liquids. Pigments and dyes produce colour in a resin due to the selective absorption of visible light with wavelengths ranging from ~380 (violet) to 760 nm (red). Because the dyes are in solution, the colour is produced only from light absorption, and the material is transparent. The colour shade is dependent on the particle size of the pigment. Ultramarine blue pigments are nonreflective due to their

refractive index, which is similar to that of the polymer. Pigments must be adequately dispersed in the polymer for optimum scattering. Specks and uneven colouration can result from incomplete dispersion. If agglomerates are present, they may adversely affect the mechanical properties (i.e., tensile strength, impact strength, and flex fatigue) of the resulting product. The pigments should be compatible with the polymer because poor compatibility may result in part failure. High temperature during processing can damage or destroy the pigment resulting in shade variation or colour loss. The thermal sensitivity is related to both temperature and duration of exposure. Long cycles during injection moulding and rotational moulding can have a more adverse effect than high-speed extrusion. Some pigments can act as nucleating agents altering the mechanical properties and improving the clarity of the polymer. The most common inorganic pigments include oxides, sulphides, hydroxides, chromates, and other complexes based on metals, such as cadmium, zinc, titanium, lead, and molybdenum. In general, they are more thermally stable than organic pigments and are more opaque and resistant to migration, chemicals, and fading. They can cause wear on the processing equipment (e.g., extrusion machine screws and barrels). The use of heavy metal compounds (e.g., cadmium) has been restricted due to toxicity issues. The most widely used white pigment is titanium oxide (rutile), which is used either alone or in combination with other colourants to control the opacity and produce pastel shades. Other white pigments include zinc oxide, zinc sulphide, and lead carbonate (lead white). The most widely used black pigment is carbon black, which is essentially composed of pure carbon. When combined with white pigments, it produces various shades of grey depending on the particle size and tinting strength of the carbon black grade. Iron oxide, Fe_3O_4 , is another black pigment that has a lower thermal stability and tinting strength. A variety of inorganic compounds are used as pigments to colour polymers. Drobný (Drobný, 2007) classified the most common types of pigments. The yellow pigments include chrome yellow, chrome-titanium yellow, iron oxides, and lead chromates. The orange pigments include molybdate orange and cadmium orange. The brown pigments include iron oxide or a combination of chrome/iron oxides. The red pigments include iron oxide and cadmium sulphide/selenide. The blue pigments include ultramarine (aluminosilicate with sodium ion and ionic sulfur groups) and mixed metal oxides that are primarily based on cobalt aluminate. The green pigments include chrome oxide and cobalt-based mixed oxides. In general, the organic pigments are brighter, stronger, and more transparent than inorganic pigments but are not as light resistant. They may be partially soluble in many polymers but exhibit a much greater tendency to migrate. The largest group of organic pigments are the azo pigments, which contain one or more azo chromophoric groups and form yellow, orange, and red pigments. Monoazo pigments, which have only one chromophore, exhibit low thermal and light stability and have a tendency to bleed. In addition, the monoazo pigments are not typically employed in plastics. Polyazo pigments, which have more than one chromophore, do not tend to bleed and have better thermal stability and excellent chemical stability. Nonazo pigments have a variety of structures including polycyclic and metal complexes. Phtalocyanine blues and greens, most of which are complexed with

copper, are highly stable to light, heat, and chemicals and form highly transparent, intense colours with a high tinting strength. Other organic pigments include quinacridones (red, violet, orange), dioxazines (violet), isoindolines (yellow, orange, red), perylenes, flavanthrones, and anthraquinones. In addition, thiazine pigments are suitable for almost all organic pigment applications (Smith, 2002). In low concentrations, thiazine pigments provide high value-in-use due to their heat stability (up to 290 -300 °C) in polyolefins enabling warpage-/deformation-free HDPE mouldings, high opacity coupled with very high colour saturation, ease of incorporation (dispersion, flow), chemical inertness, high insolubility in nearly all solvents, high performance in the intended applications (processability and durability), ability to form supramolecules with synergistic values, potential environmental compatibility, and cheap cost.

3. Experimental

3.1. Characterization and preparation pigment and pigment composites

The silicas used as the support medium of composite pigments in these studies are as follows: Aerosil 380 (Degussa S.A.) – a hydrophilic fumed silica with a specific surface area of 340 - 380 m²/g; Zeosil 175 (Rhodia) – a precipitated silica with a specific surface area of 175 m²/g; Silica Gel 60 (Merck) – a silica with a specific surface area of 470 – 540 m²/g. The indigothiazine pigment was used as the coloured chromophore. Below 180 °C, the *cis* form of this pigment is yellow in colour and transforms into the highly durable *trans* form characterised by the red colour upon heating (Figure 1). The latter form is highly resistant to organic solvents, high temperatures, and light. The *cis* form of indigothiazine was obtained by according to the description in the patent Bansil Lal (Bansil Lal et al., 2002).

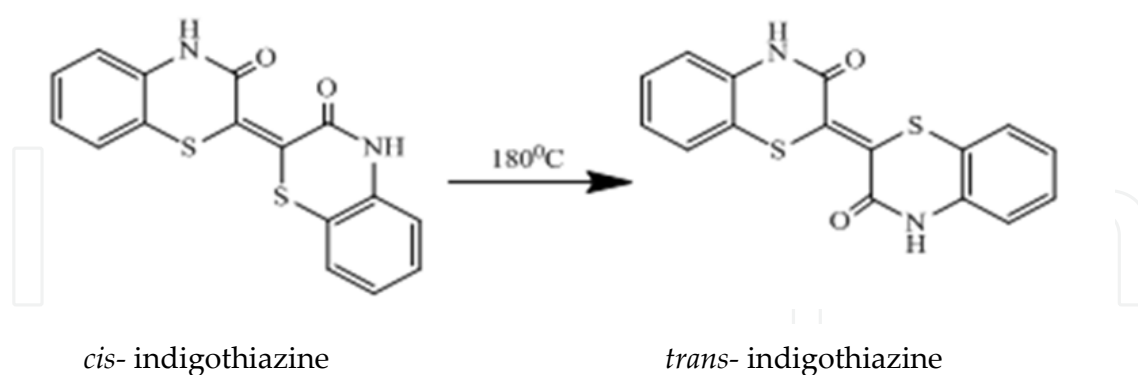


Figure 1. Isomeric conversion of *cis*- to *trans*-indigothiazine – ([2,2']-bi(1,4-benzothiazynylidene)-3,3'-(4H, 4'H)-dione.

3.2. Characterisation and preparation pigment and pigment composites

The composite pigments were prepared by mechanically applying *cis*-indigothiazine on silica surfaces and subjecting them 180 °C for 2 h to induce their transformation into the

highly durable *trans* form. The mechanical application of the *cis* form on silica was accomplished by means of a high-speed blender (Warning Commercial) at ~14,000 rpm. The quantity of the pigment was measured relative to the weight of silica, and the modification required 15 min (Fig. 2).

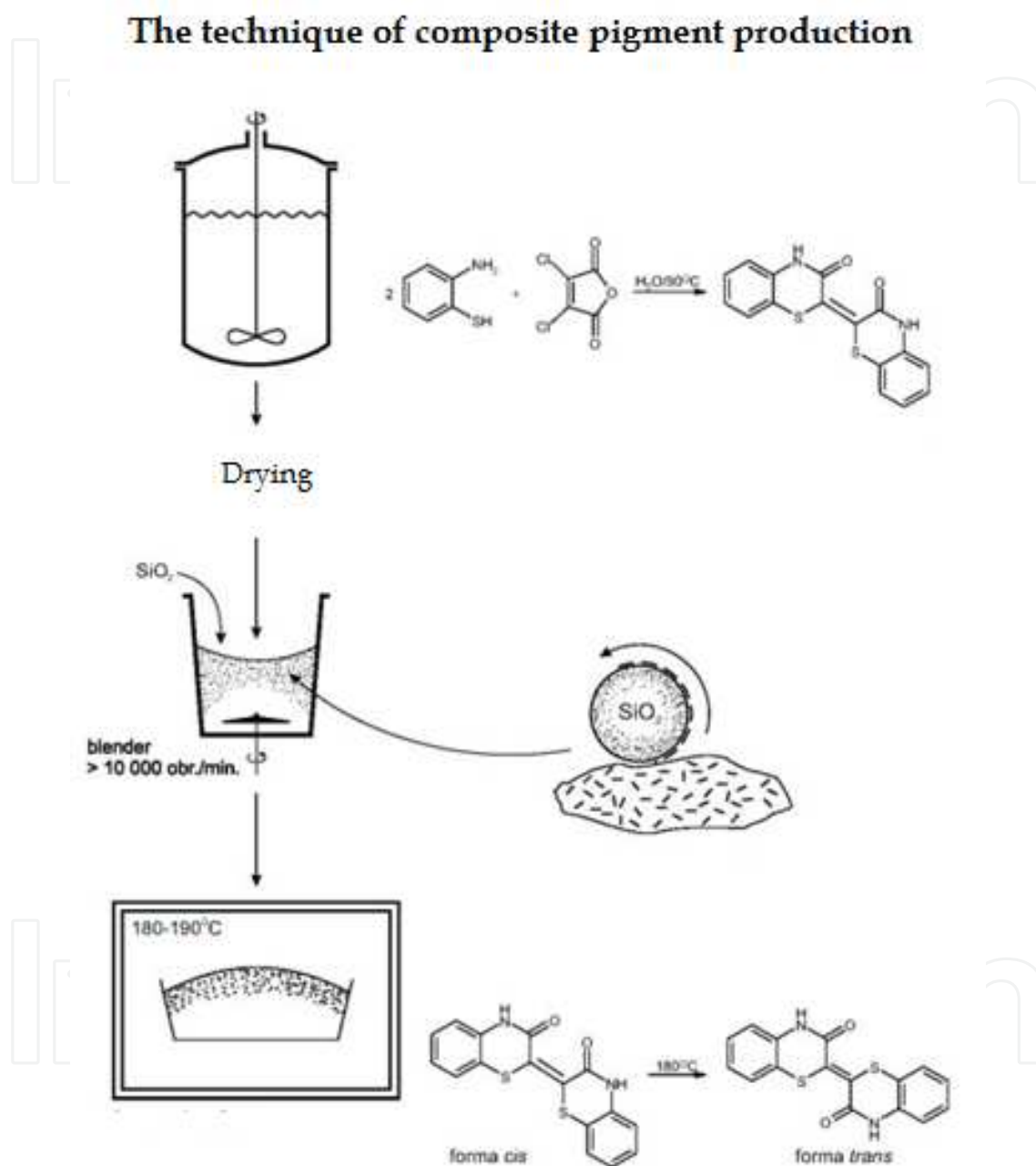


Figure 2. Production process scheme of composite pigments (Copyright Lipińska et al. 2011).

To assess the mechanism and kinetics of the electrochemical oxidation of the compounds under investigation, cyclic voltammetry (CV) and differential pulse (DPV) methods were employed on an Autolab analytical unit (EcoChemie, Holland). A three-electrode system was employed for the measurements. Platinum was used as the anode and the auxiliary

electrode. The potential of the tested electrode was measured versus a ferricinium/ferrocene reference electrode (Fc⁺/Fc) where the standard potential is defined as zero and independent of the solvent used. Prior to the measurements, all of the solutions were deoxygenated with argon. During the measurements, an argon atmosphere was maintained over the solution. The effect of the scan rate on the electrooxidation of indigothiazine in an anhydrous medium was investigated. The differential scanning calorimeter (DSC) measurements of *cis*- and *trans*-indigothiazine and vulcanisates were performed on a DSC1 calorimeter (Mettler Toledo) with a heating rate of 10 °C/min. The morphology of the indigothiazine particles and the dispersion in the elastomer matrix containing either unmodified silica or the composite pigments was estimated using scanning electron microscopy with a LEO 1530 SEM microscope. The NBR vulcanisates were broken down in liquid nitrogen, and the fracture surfaces of the vulcanisate were examined. Prior to the measurements, the samples were coated with carbon. The prepared pigment composites were characterised to evaluate the agglomerate size distribution in the water medium using dynamic light scattering (Zetasizer Nano S90, Malvern) for a dispersion concentration of 0.2 g/l (the powders were pre-treated with ultrasound for 0.5 h). The specific surface area of the silica fillers before and after application of indigothiazine was determined. The measurements were performed using the Brunauer-Emmet-Teller (BET) nitrogen adsorption method (GEMINI 2360 V2.01). The zeta potential of the silicas and of pigment composite were evaluated (ZETASIZER 2000, the water dispersion with concentration 2 g/l). The powders were pre-treated with ultrasound for 1 h.

3.3. Preparation and vulcanization of rubber compounds

The composite pigments were used as the rubber mixture fillers. The rubber mixture composition was made up of the following: NBR (Perbunan 28-45F containing 28 wt % acrylonitrile groups from Lanxess, 100 phr); sulphur crosslinking system (See Table 2) and optional: composite pigments or silica (30 phr).

The mixture composition	^a phr
NBR rubber	100
Zinc oxide	5
Sulphur	2
Mercaptobenzothiazole	2
Stearic acid	1
Filler	30

^aphr = parts per hundred of rubber by weight

Table 2. Rubber formulations.

The mixture was prepared in a laboratory rolling mill (Roll dimensions: D = 200 mm, L = 450), and the vulcanisation process was carried out in a hydraulic press (160 °C) in line with the curing time specifications (See Table 2). The vulcanisation kinetics was measured with evaluated using a Monsanto vulcameter with an oscillating rotor (ZACH Metalchem) in

compliance with the ISO-4317 standard. The tests performed on the vulcanizates are summarised as follows: the mechanical properties were characterised using a Zwick 1435 strength testing machine and according to ISO-37. The crosslink density of vulcanizates was determined by equilibrium swelling in toluene, based on the Flory-Rehner (Flory et al., 1943) equation using the Huggins parameter of elastomer–solvent interaction $\mu = 0.381 + 0.671V_r$ [eq. (1)].

$$v_e = - \frac{\ln(1-V_r)V_r + \mu V_r^2}{V_0(V_r^{\frac{1}{3}} - \frac{V_r}{2})} \quad (1)$$

where: v_e - crosslink density, V_r - volume fraction of elastomer in swollen gel, V_0 - molar volume of solvent [mol/cm³].

spectrophotometric data were taken using a KONICA–MINOLTA CM–3600 spectrophotometer under computer control with spectra analysis software (Colour Data Software CM – S 100 in Spectra Magic) according to the following standards: CIE No. 15; PN-EN ISO 105- J01; ASTM E1 164; and DIN 5033 Tell.7, resistance to ageing under UV radiation was tested by exposing the vulcanizates to a UV source (Atlas UV200) for a total of 5 days, equivalent to the ageing by approximately 3 months under normal conditions. The test timeline was as follows: day segment: UV power 0.7 W/m²; temperature 60 °C; duration 8 h, night segment: UV power 0.0 W/m²; temperature 50 °C; duration 4 h. The vulcanizates subjected to UV ageing were tested for tensile strength. Spectrophotometric measurements were performed before and after UV irradiation. For each vulcanizate being tested, the ageing coefficient, K , was computed using Equation 2:

$$K = \frac{(TS \cdot Eb)_{\text{after ageing}}}{(TS \cdot Eb)_{\text{before ageing}}} \quad (2)$$

where: K – ageing coefficients; TS – tensile strength; Eb – relative elongation.

4. Results

The electrode reactions characterising the electrochemical oxidation of indigothiazine at the platinum electrode were studied by cyclic pulse voltammetry. The half-wave potential of the peak in the cyclic voltammogram is characteristic of each subsequent step in the investigated electrode reaction. Selected cyclic voltammograms recorded in a solution consisting of the indigothiazine and the supporting electrolyte are presented in Fig. 3. The cyclic voltammograms recorded for the indigothiazine solution exhibit two peaks, which involve at least three electrode steps of the pigment electrooxidation in the potential range prior to the potential at which electrolyte decomposition is initiated. The supporting electrolyte (in *N*-methyl-2-pyrrolidone) has no characteristic peaks except for charging the electrical double layer. The electrooxidation potentials were determined following: the first peak - 0.71 V, second peak - 0.82 V, third peak - 1.01 V. In addition, the electrode reactions of the examined connection are becoming more and more irreparable. Polarisation towards the negative potentials of the reduction reaction was not observed (Fig. 4). The recorded voltammograms, under the linear diffusion of the first electrooxidation step, were employed to determine the half-wave potential ($E_{1/2}$). Based on the

results provided in Table 3, indigothiazine, $E_{1/2} = 0.36\text{ V}$, was easily oxidised. The energy of the highest filled molecular orbital (EHOMO) was estimated to determine the ease of electron back-donation (potential of the ionisation) and the enthalpy (ΔH). The EHOMO energy (-7.65 eV) and enthalpy (22.83) confirmed the good antioxidant properties and stability.

Compound	$E_{1/2}, \text{V}$	$E_{\text{HOMO}}, \text{eV}$	$\Delta H, \text{kcal/mol}$
Indigothiazine	0.85	- 7.65	22.83

Table 3. Cyclic voltammetry and molecular orbital parameters for the studied compound

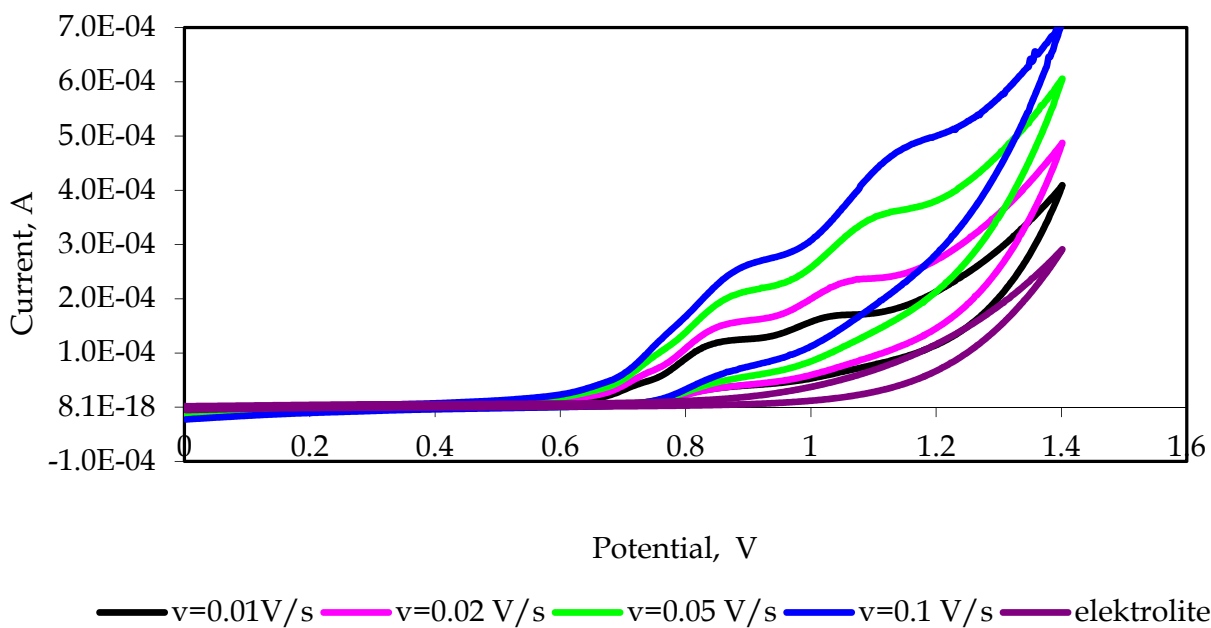


Figure 3. Voltammogram of indigothiazine oxidation on a Pt electrode; $c = 1\text{ mmol/dm}^3$ in 0.1 mol/dm^3 in *N*-methyl-2-pyrrolidone at various polarisation speeds.

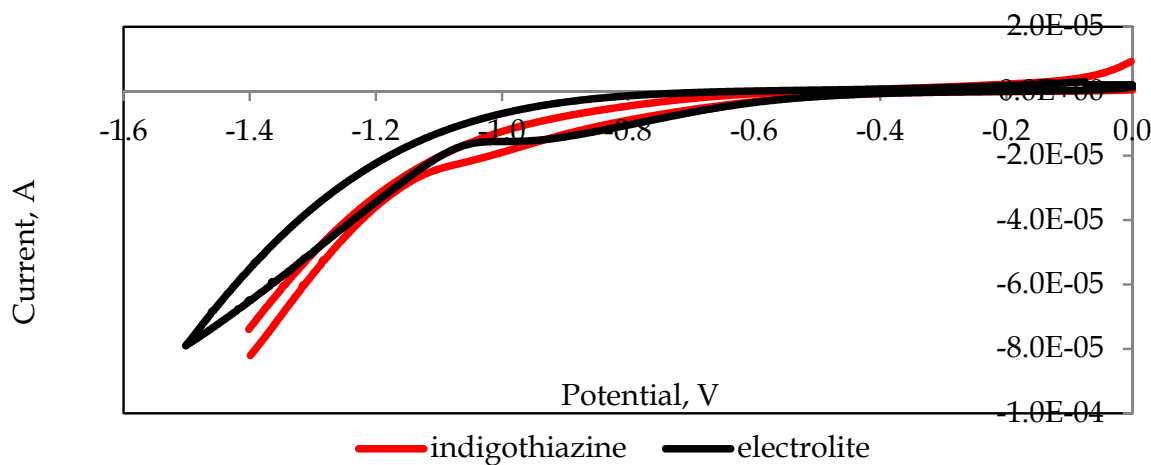


Figure 4. Voltammogram of indigothiazine for negative potential on the Pt electrode; $c = 1\text{ mmol/dm}^3$ in 0.1 mol/dm^3 in *N*-methyl-2-pyrrolidone.

The thermal strength of *cis* – and *trans*– indigothiazine (Fig.6) was measured applying the DSC method (DSC 1 Mettler Toledo). The resulting diagrams show the melting bands of the pigment's crystalline phase at around 440° C (Fig. 5). The exothermic peak on the *cis*–indigothiazine curve is in the regime where the *cis*- to *trans*- conversion took place most intensively.

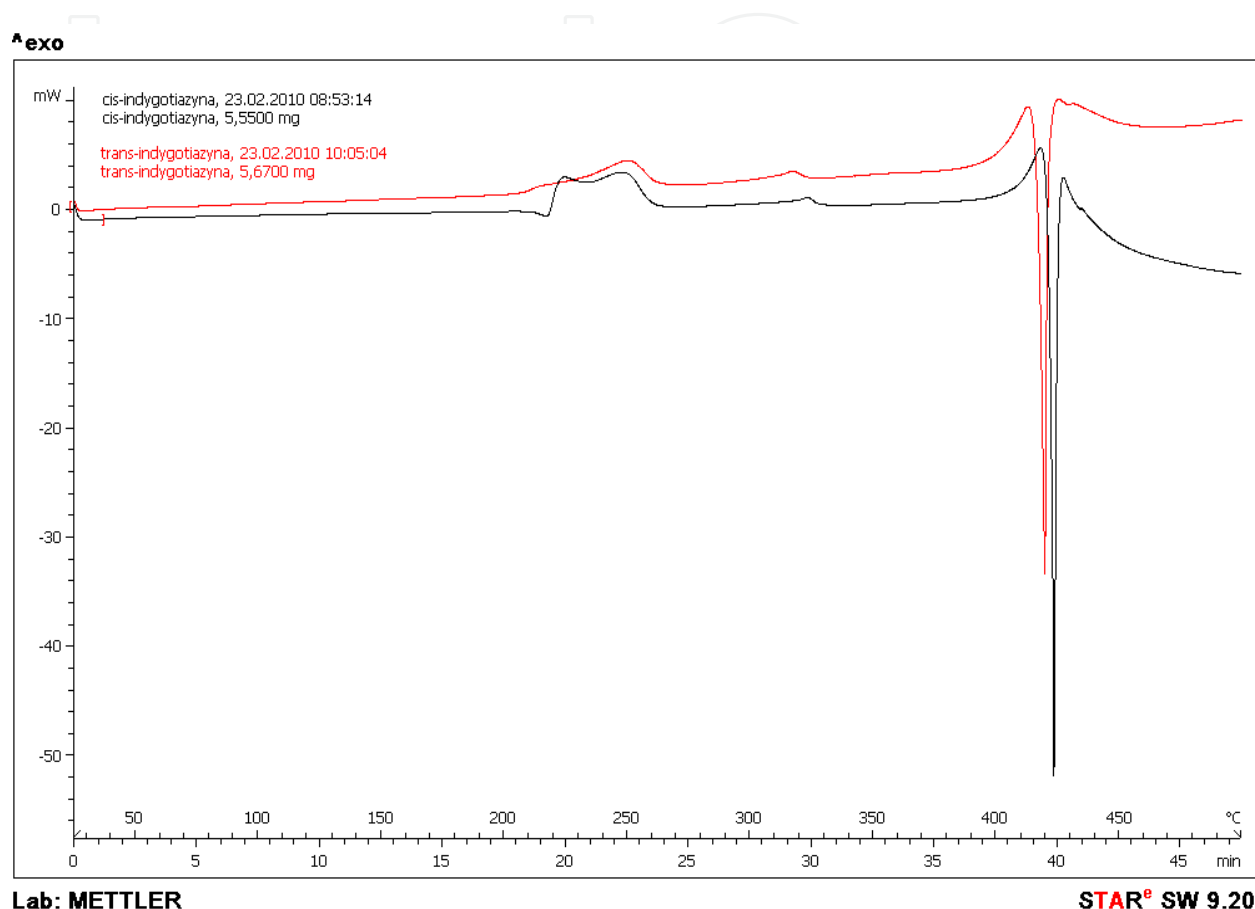


Figure 5. DSC curves of indigothiazine pigment – *cis* and *trans* conformation.

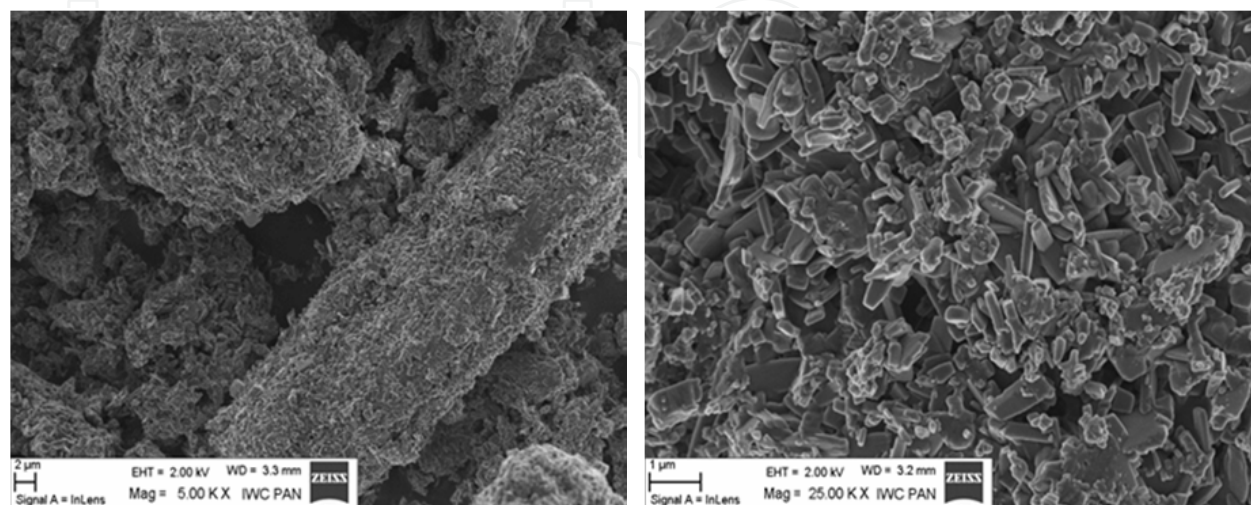


Figure 6. SEM image of trans-indigothiazine pigment .

The fumed silica, Aerosil 380, used in the tests is characterised by the high numerical percentage (99.67 %) of aggregates in the range of 116-330 nm in size; however, these aggregates account for only 28.83 % of the filler's volume in the water medium. The outstanding fraction (71.17 %) consists of agglomerates whose sizes are in the range of 1056-3000 nm. The application of indigothiazine pigment on the surface of Aerosil 380 silica reduced the average particle size and fragmented agglomerates, effectively producing the composite pigments with sizes ranging from 82-131 nm (100 %). For the precipitated silica, Zeosil 175, the application of pigment helped produce the composite pigments with 99.92 % of the aggregates in the size range from 116-262 nm and the rest the size range of 2379-3000 nm. Although the modification of Zeosil 175 reduced the average particle size and increased the particles uniformity, the particles still formed agglomerates in the order of a few μm in size. For Silica Gel 60, applying indigothiazine only slightly increased the particles tendency to agglomerate; that is, the aggregates size increased from 104-147 nm (unmodified) to 116-208 nm (modified). The results are summarized in Table 4.

Aggregates name	Aggregates size [nm]	Numerical percentage [%]	Volumetric percentage [%]	BET [m^2/g]
A 380 (Aerosil 380)	116 - 330	99.67	28.83	246
	1056 - 3000	0.33	71.17	
A 380/ indigothiazine	82 - 131	100	100	185
Z 175 (Zeosil 175)	147 - 234	89.24	61.68	187
	330 - 527	10.75	33.13	
	2379 -3000	0.01	5.19	
Z175/ indigothiazine	116 - 262	99.92	34.85	131
	2379 - 3000	0.08	65.15	
S 60 (Silica Gel 60)	104 - 147	100	100	526
S60/ indigothiazine	116 - 208	100	100	396

Table 4. Aggregates size and specific surface area of the silicas and composite pigments.

The specific surface area was measured using the BET nitrogen adsorption method before and after applying the indigothiazine pigment. Each composite pigment was characterised by reduced specific surface area as compared with the unmodified silicas. The decrease in the specific surface proceeded to a larger extent in the case of Aerosil 380 and Silica Gel 60 with a large specific surface.

Figures 7-9 shows the change in zeta potential as a function of pH for both unmodified silicas and composite pigments. The largest change in the surface charge was caused by the application of indigothiazine to Zeosil 175 silica. The difference in zeta potential between the composite and unmodified silica Zeosil 175 was approximately 30 mV (pH 4), indicating that the modification reduced the acidic characteristics of the Zeosil 175 surface, which is a favourable result for its use as a polymer composite filler. For the A 380/ indigothiazine pigment, the zeta potential was slightly higher than for the unmodified Aerosil 380. For Silica Gel 60 and the Silica Gel 60/ indigothiazine composite, the two zeta potential curves overlapped one another, indicating that the application of the pigment induced practically no change to the surface charge in this filler.

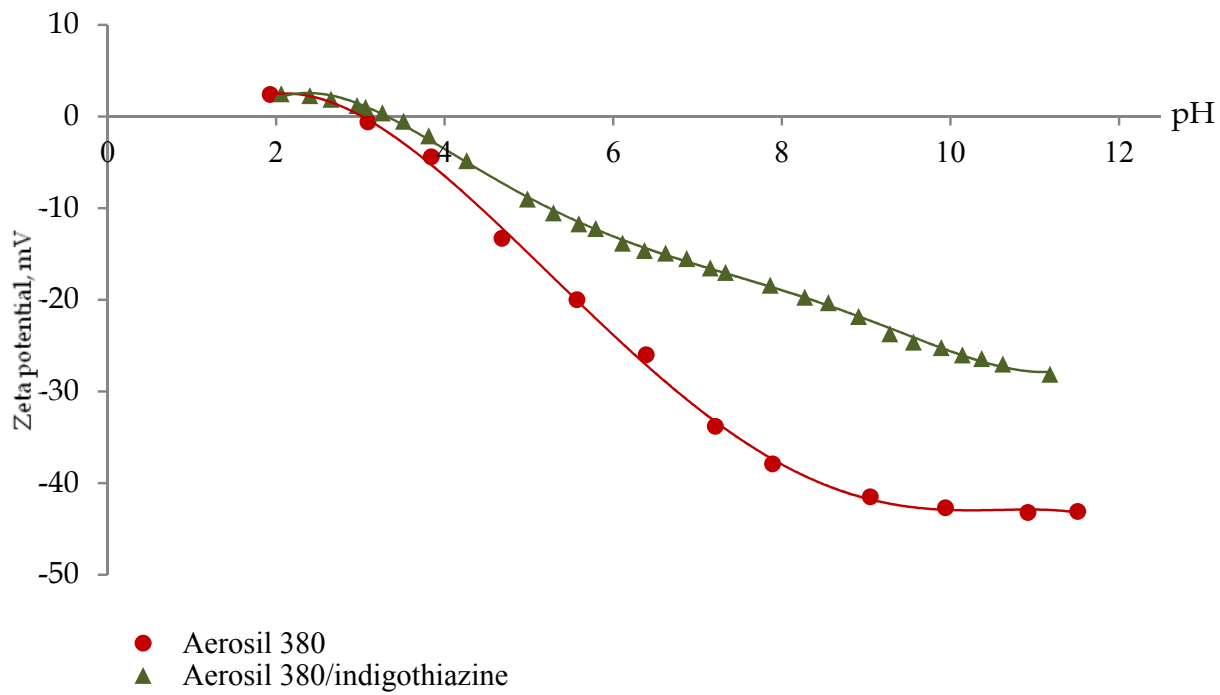


Figure 7. Zeta potential diagram for the composite pigments in which the supports was Aerosil 380.

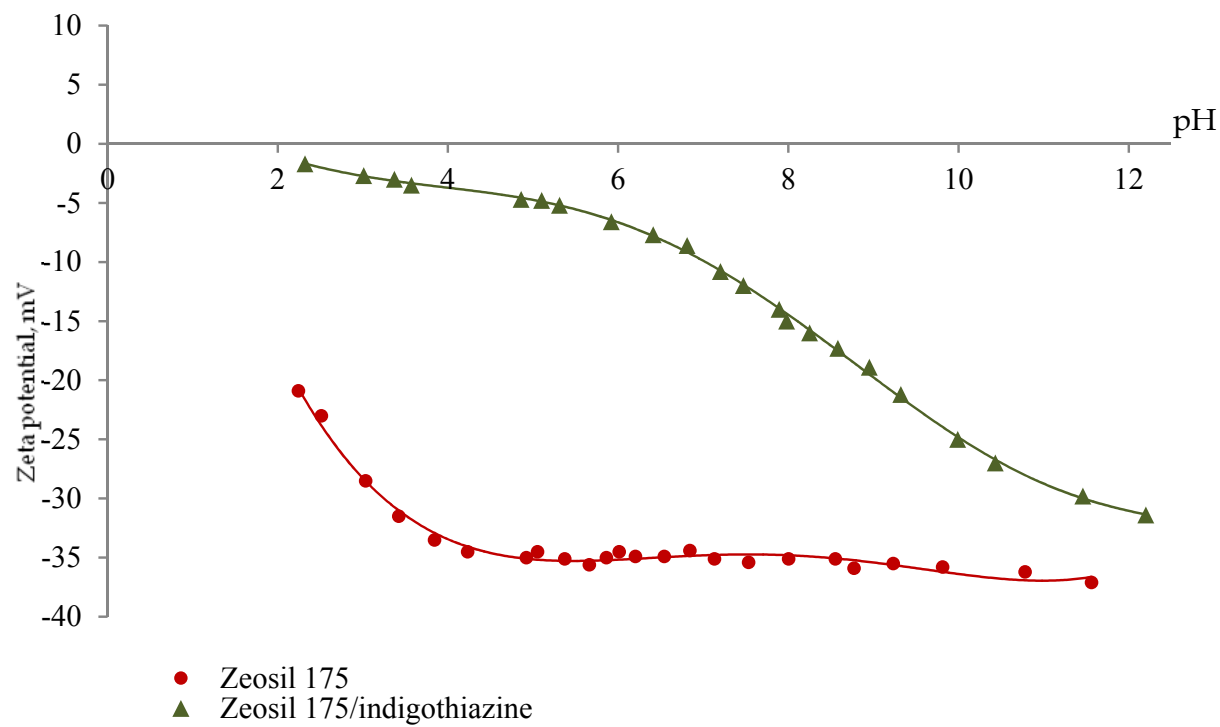


Figure 8. Zeta potential diagram for the composite pigments in which the support was Zeosil 175.

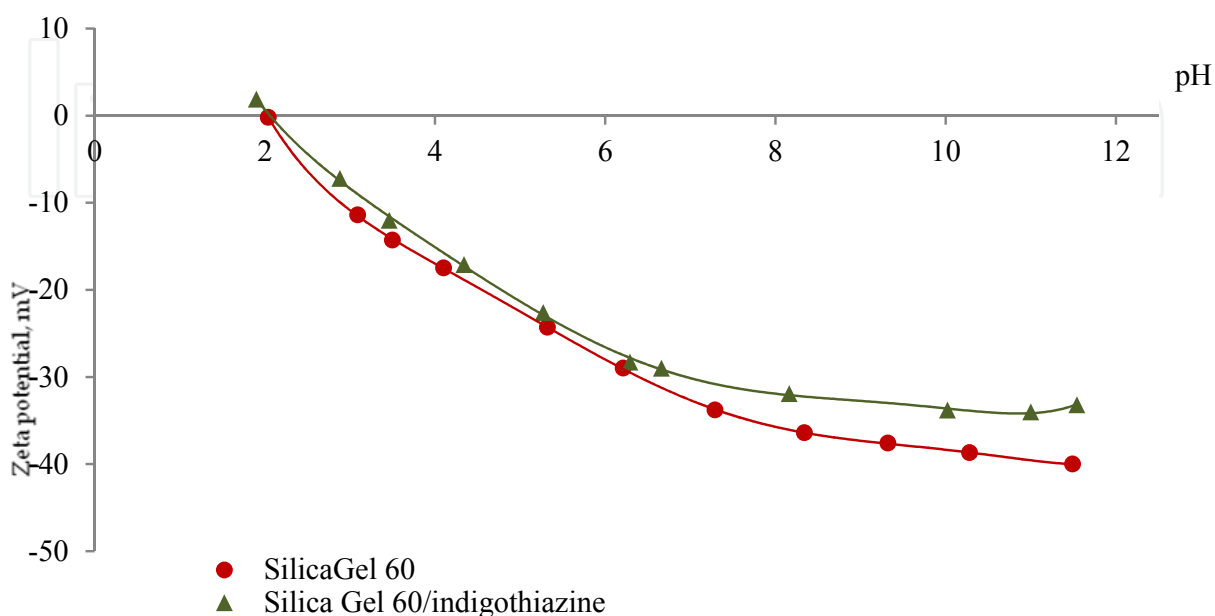


Figure 9. Zeta potential diagram for the composite pigments in which the support was Silica Gel 60.

The effects of silicas and the composite pigments on the properties of rubber mixtures were evaluated with respect to the curing kinetics and tensile strength of the vulcanizates (Table 5). Rheometric tests showed that adding composite pigments to the rubber mixture did not significantly affect the vulcanisation time, t_{09} , torque increase, ΔM , and the initial viscosity values (M_{\min}) in comparison to the mixtures containing unmodified silicas. The only exception was the Zeosil 175/ indigothiazine composite, which showed a lower torque increase than the original Zeosil 175. Tg values from DSC curves for vulcanizates filled modified and unmodified silicas have similar glass transition temperature in range -28°C – 30°C (Table 5). The vulcanisation process produced red-coloured vulcanizates, which were then subjected to tensile strength tests. The results showed that the application of the composite pigments had a similar effect on the mechanical properties of the vulcanizates as did the application of the unmodified fillers, as indicated by the tensile strength TS (Table 5) and the Scanning Electron Microscope SEM observations. The SEM images revealed agglomerates in the vulcanizates filled with unmodified silicas (Figs. 11, 13, 15) and composite pigments (Figs. 12, 14, 16). Even though the modification of the test fillers reduced the average size of agglomerates in the water medium, it did not significantly affect the dispersion level of silicas in the elastomer. The vulcanizates containing modified silicas had also similar values of curing density, module values at 100% stress and elongations at break EB in comparison to composites filled unmodified silicas.

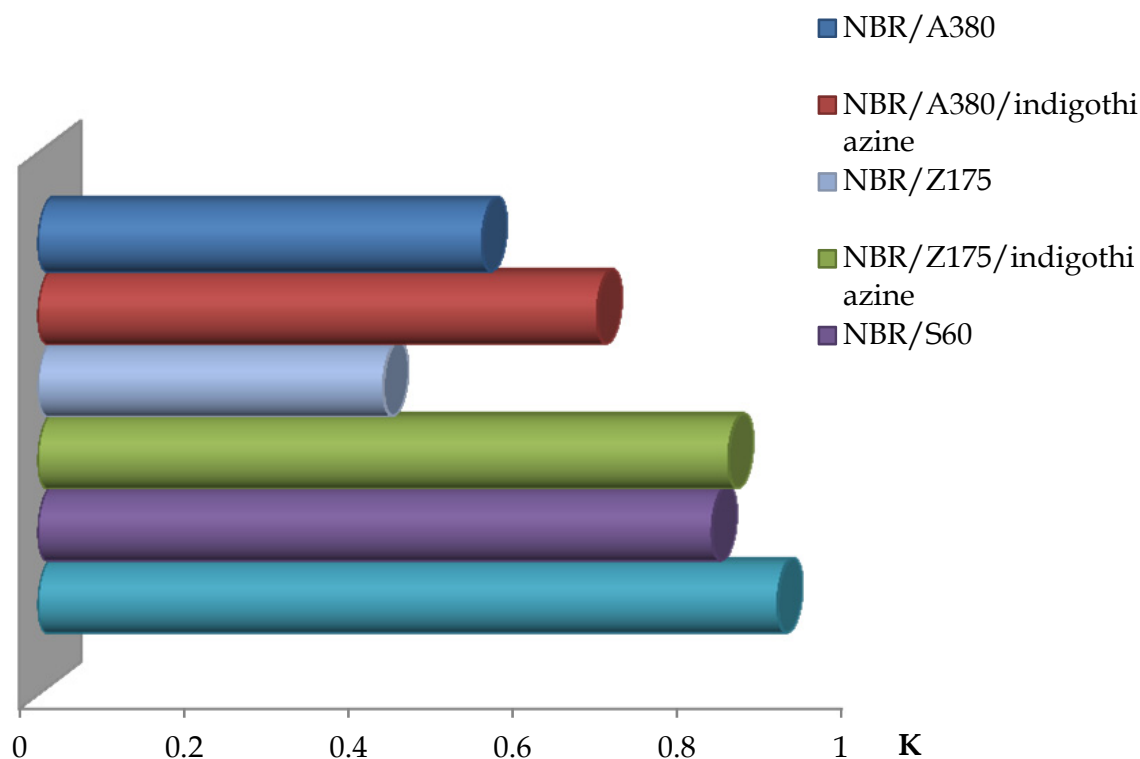


Figure 10. Ageing coefficient value (K) of vulcanizates filled with composite pigments and unmodified silicas.

Next, the functional properties of the vulcanizates after undergoing the 120 h of UV ageing were re-examined. After ageing, all samples exhibited lower TS and EB values and a higher curing density; however, the vulcanizates containing either the A 380/ indigothiazine, Z 175/ indigothiazine and S60/ indigothiazine composites exhibited less UV degradation. Based on the K values (Fig.10), it is possible to conclude that the pigment protects against ageing most effectively when applied to the A380 and Z175 silica supports. The closer the K value is to unity, the less ageing is considered to have taken place. Colorimetric tests of the aged vulcanizates were also performed using the non-aged samples as benchmarks (Table 6). The colorimetric measurements were taken in the CIE-Lab space that expressed the colours in the Cartesian L-a-b coordinate system of the brightness L, the red-greenness a, and the yellow-blueness b. The L value ranges from 0 (black) to 100 (white), and all shades of grey are expressible by the values in between. The colorimetric data reveal that the UV radiation not only degrades the functional properties but also changes the colour of the vulcanizates (Table 6). The parameter dE^*ab depicts the degree of change in colour as a result of ageing. All the vulcanizates containing composite pigments exhibited a lesser degree of change in colour than those containing unmodified silica. The vulcanizates with either the A 380/ indigothiazine composite or the Silica Gel 60/ indigothiazine composite exhibited three times less the degree of change in colour than those with ordinary silicas.

Mixture symbol	M_{\min} [dNm]	ΔM [dNm]	t_{09} [min]	Sample condition	SE_{100} [MPa]	TS [MPa]	E_b [%]	$v_e \cdot 10^{-5}$ [mol/cm ³]	DSC [°C]
NBR/ A 380	31	112	27.0	non-aged	1,74	17,6	614	5,41	-29
				UV aged	2,87	10,5	564	6,48	
NBR/ A 380/ indigothiazine	31	109	30.0	non-aged	1,87	17,1	677	5,44	-28
				UV aged	2,52	12,12	652	6,34	
NBR/ Z 175	32	134	25.0	non-aged	1,69	15,3	619	5,75	-30
				UV aged	2,38	7,85	510	6,54	
NBR/ Z 175/ indigothiazine	25	132	22.8	non-aged	1,53	16,7	628	5,69	-28
				UV aged	2,22	14,2	617	6,41	
NBR/ S 60	29	89	11.9	non-aged	1,73	4,39	466	6,12	-28
				UV aged	1,94	4,06	413	7,05	
NBR/ S 60/ indigothiazine	28	98	14.6	non-aged	2,42	4,52	248	7,89	-29
				UV aged	2,92	4,46	226	9,05	

M_{\min} – minimum torque [dNm], ΔM – torque increase [dNm], t_{09} – vulcanisation time [min], SE_{100} – stress at 100 % elongation [MPa], TS – tensile strength [MPa], E_b – relative elongation at break [%], v_e – curing density of vulcanizates calculated using the Flory Rehner equation [mol/cm³]

Table 5. Effects of composite pigments and unmodified silicas on selected properties of NBR.

Sample name Rubber/silica/pigment	dE*ab	L*	a*	b*	dl*	da*	db*
NBR/ A380 (benchmark)	-	71.77	2.31	16.80	-	-	-
A 380 UV	30.70	53.03	12.82	38.73	-18.74	10.51	21.93
NBR/A 380/ indigothiazine (benchmark)	-	46.09	46.97	35.58	-	-	-
NBR /A 380/ indigothiazine UV	9.48	38.05	43.03	38.68	-8.05	-3.93	3.10
NBR/Z 175 (benchmark)	-	73.09	1.65	21.84	-	-	-
NBR/Z 175 UV	29.52	52.77	13.48	39.71	-20.31	11.83	17.86
NBR/Z175/ indigothiazine (benchmark)	-	46.66	52.13	42.95	-	-	-
NBR/Z175/ indigothiazine UV	17.40	40.50	40.32	31.76	-6.16	-11.81	-11.19
NBR/Silica Gel 60 (benchmark)	-	66.86	3.08	15.76	-	-	-
NBR/Silica Gel 60 UV	30.44	52.99	14.07	40.52	-13.88	10.99	24.76
NBR/Silica Gel60/ indigothiazine (benchmark)	-	48.28	43.64	29.66	-	-	-
NBR/Silica Gel 60/ indigothiazine UV	9.19	40.75	40.78	34.07	-7.54	-2.86	4.41

L* – brightness parameter, a* – redness – greenness reading, b* – yellowness – blueness reading, dl*, da*, db* – the difference in colour between trial and standard readings; dE*ab – vector of overall errors in colour and colour darkness;

Table 6. Colorimetric data for the vulcanizates containing unmodified silicas or composite pigment.

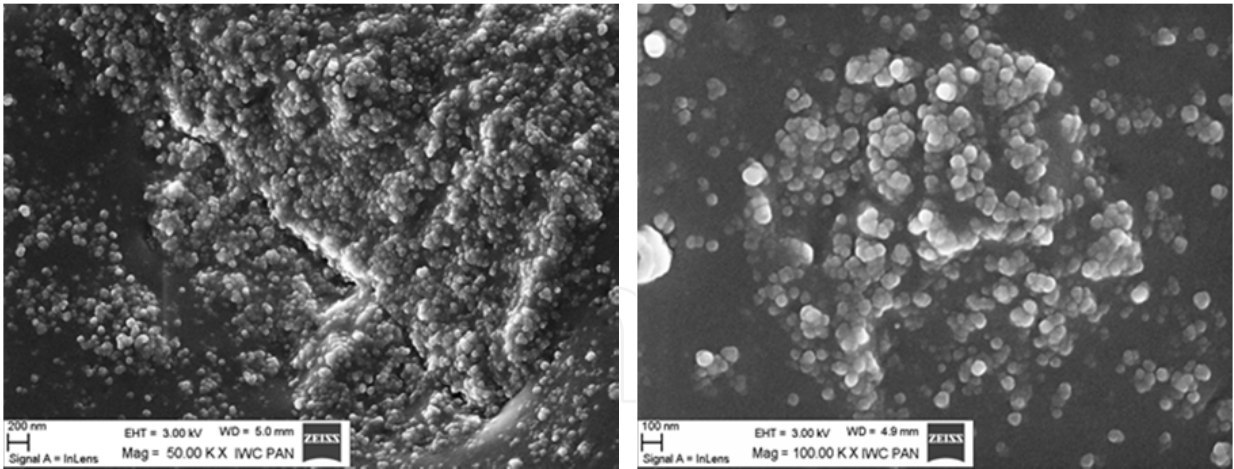


Figure 11. SEM image of NBR vulcanizate filled with Aerosil 380.

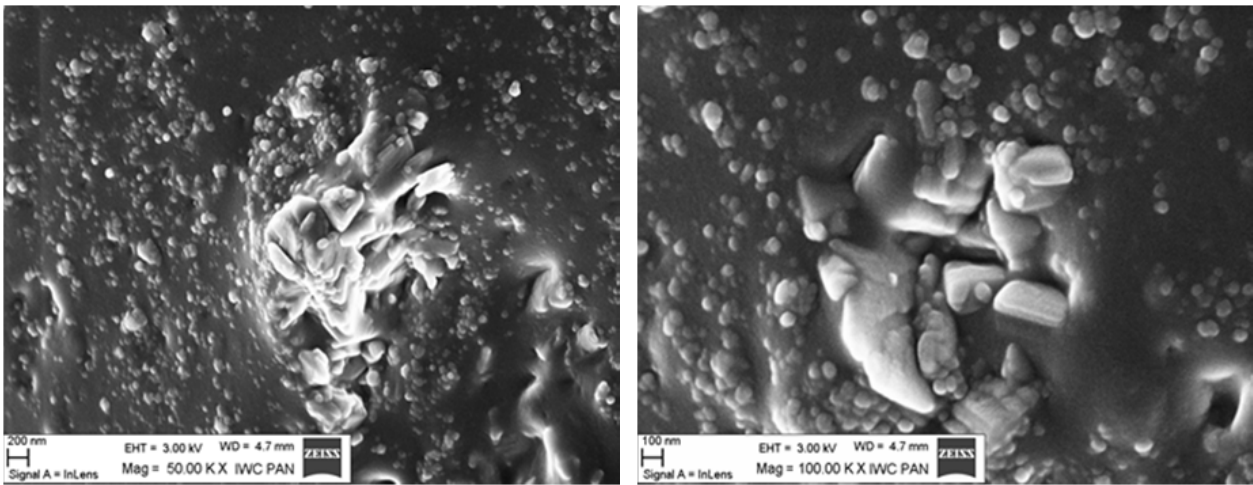


Figure 12. SEM image of NBR vulcanizate filled with A 380/indigothiazine.

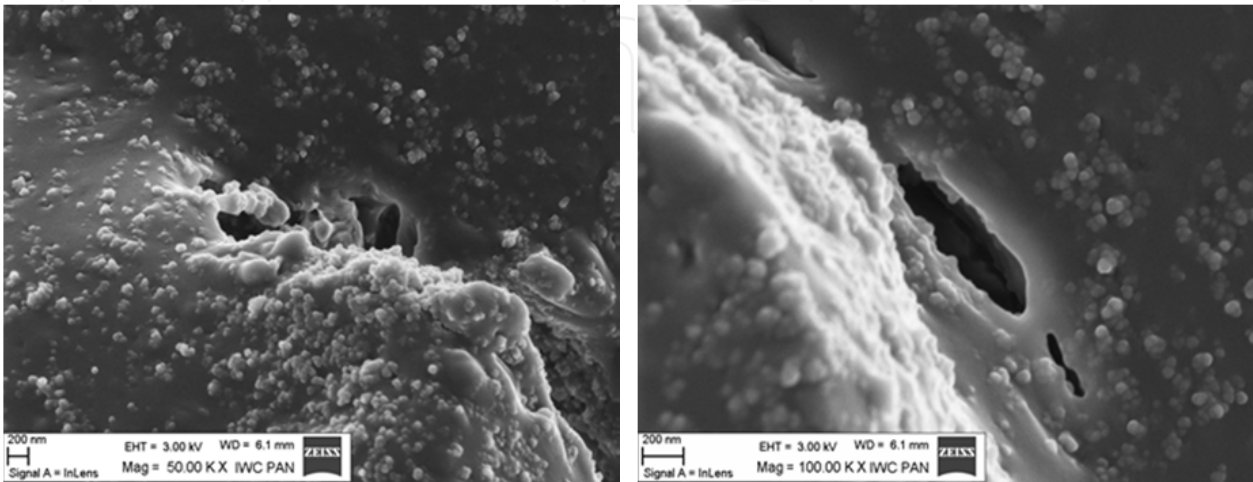


Figure 13. SEM image of NBR vulcanizate filled with Zeosil 175.

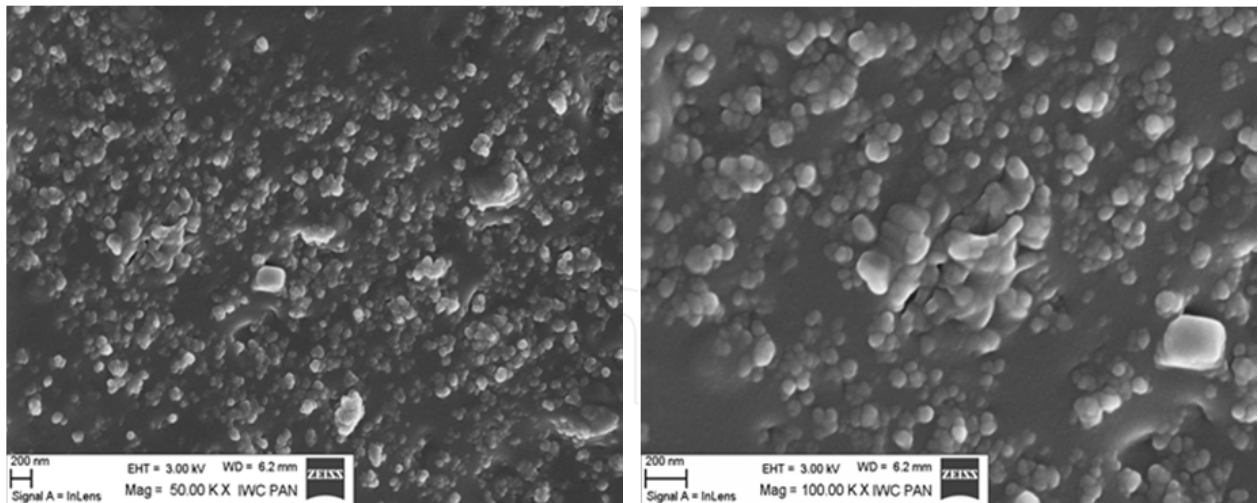


Figure 14. SEM image of NBR vulcanizate filled with Z 175/indigothiazine.

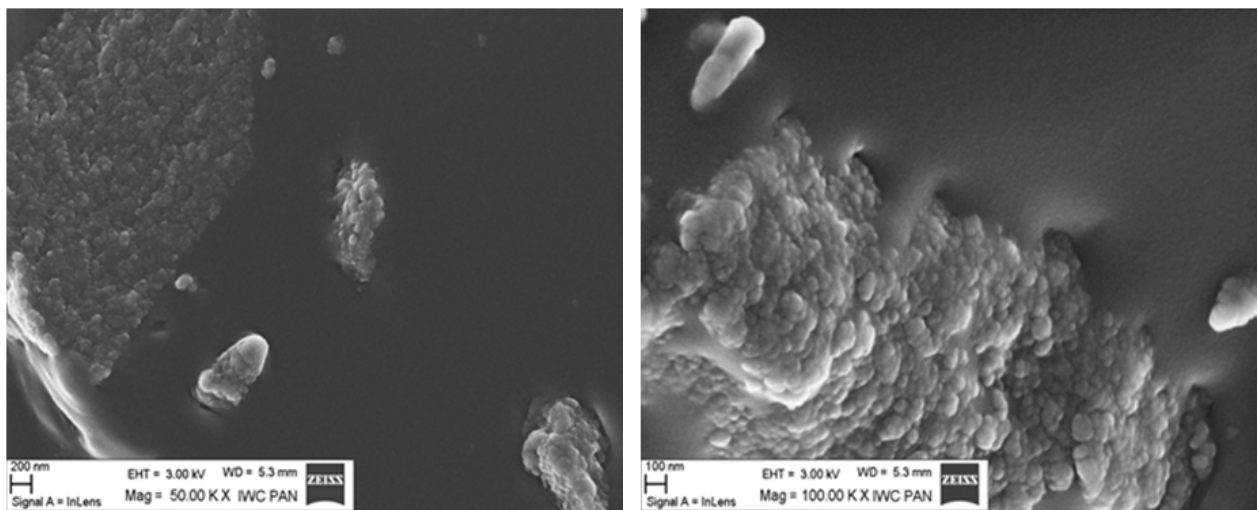


Figure 15. SEM image of NBR vulcanizate filled with Silica Gel 60.

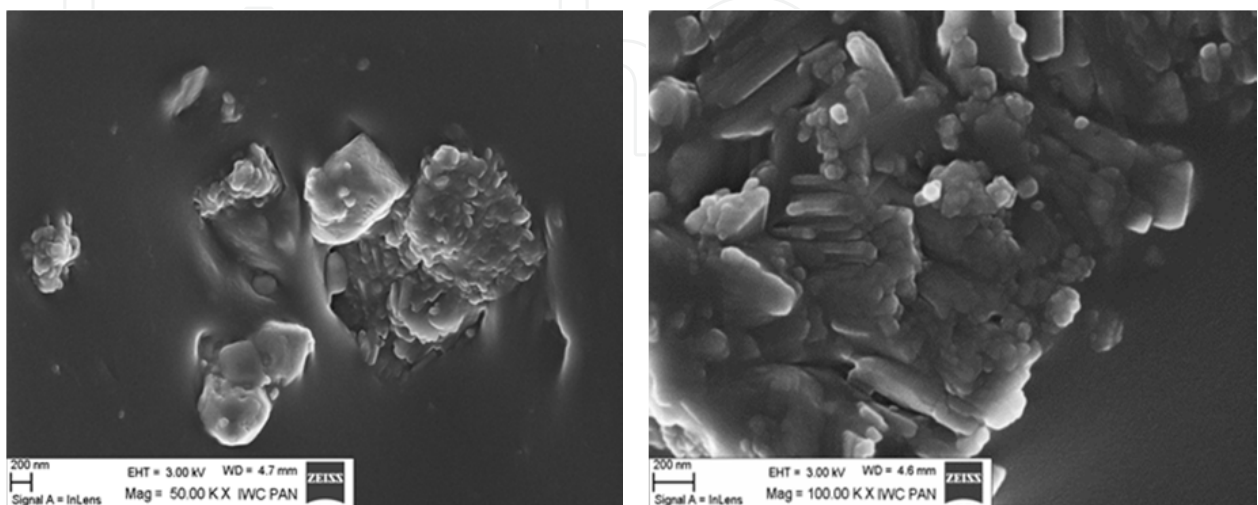


Figure 16. SEM image of NBR vulcanizate filled with S60/indigothiazine.

5. Conclusions

Indigothiazine exhibited antioxidant properties, which allows them to be successfully employed as anti-ageing substances. Red-colour composite pigments were produced by modifying silica Aerosil 380, Zeosil 175, and Gel 60. The modification method employed in the present work eliminated harmful solvents employed in the conventional process. The newly developed method is much simpler, cheaper, and easier to use on an industrial scale compared to the conventional process, which requires a solvent. The silica modification process using the blender reduced the specific surface area of the tested fillers. For the composites with Aerosil 380, Zeosil 175 and Silica Gel 60, this process reduced the agglomerate sizes. For the samples with Aerosil 380 and Zeosil 175, the zeta potential also increased, which indicated that their surface became less polarised and their acceptor characteristic was partially lost. The addition of the composite pigments to the polymer mixtures did not significantly change their curing kinetics or processing properties. The vulcanisation of NBR in the presence of the modified silicas resulted in vulcanisates with a vivid red colour were produced. Vulcanisates filled with the composite pigments and those filled with unmodified silicas exhibited similar mechanical strengths. The strength tests after UV ageing of the vulcanisates showed that the A 380/indigothiazine composite and the Zeosil 175/indigothiazine composite possess anti-ageing properties and have a favourable impact on the plastic's mechanical properties and colour stability. The present work led to the successful production of vulcanisates with enhanced ageing resistance.

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