# SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

**1. NAME AND SURNAME: Urszula Szeluga**

**2. DIPLOMAS AND SCIENTIFIC DEGREES:**

September 1996      **Master of Sciences,** specialization Chemical Technology
Faculty of Chemistry, Silesian University of Technology, Gliwice

Diploma thesis: „Study of 2-isopropylnaphtalene oxidation with molecular oxygen in emulsion with an aqueous NaOH solution with copper catalysts towards 2-isopropylnaphtalene hydroperoxide"

Supervisor: dr. Zbigniew Stec

June 2006      **Doctor of Chemical Sciences**, specialization Chemical Technology,  Chemistry and Technology of Polymers
Faculty of Chemistry, Rzeszów University of Technology

Ph.D. thesis: „Modified epoxy matrices to composites with improved thermal resistance"

Supervisor:  prof. Henryk Galina

**3. INFORMATION ABOUT PAST AND CURRENT EMPLOYEMENT IN SCIENTIFIC INSTITUTIONS:**

1996-2006      Institute of Carbon Chemistry, Polish Academy of Sciences, Gliwice

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|---|---|
| September 1996 - November 1996 | trainee in Laboratory of Non-Energetic Use of Coal |
| December 1996 - November 1999 | chemical engineer in Laboratory of Non-Energetic Use of Coal |
| December 1999 - June 2007 | assistant in Laboratory of Non-Energetic Use of Coal |

2007 to date      Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze

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|---|---|
| July 2007 - November 2016 | assistant professor in Laboratory of Carbon and Polymer-Carbon Materials |
| November 2016 to date | specialist in Laboratory of Carbon and Polymer-Carbon Materials |

**4. PRESENTATION OF THE SCIENTIFIC ACHIEVEMENT**

**a) TITLE OF SCIENTIFIC ACHIEVEMENT:**

The scientific achievement resulting from article 16.2 of march 14 2003 about scientific degree and scientific titles and degrees and titles in the field of art (act no. 65, item 595 as amended), which I present as a habilitation thesis is a monothematic series of publications titled:

 **"EFFECT OF POLYMER MATRIX AND CARBON FILLER STRUCTURES ON THE MORPHOLOGY AND PROPERTIES OF POLYMER-CARBON COMPOSITES"**

**b)** **LIST OF ARTICLES CONSTITUTING THE SCIENTIFIC ACHIEVEMENT OF CANDIDATE TO HABILITATION (AUTHORS, TITLES, YEAR OF PUBLICATION, NAME OF JOURNAL) IN CHRONOLOGICAL ORDER WITH IF, POINTS AWARDED BY THE MINISTRY OF SCIENCE AND HIGHER EDUCATION OF POLAND (MNISW) AND THE CONTRIBUTION OF THE CANDIDATE:**

**H1**. **U. Szeluga,**\* L. Kurzeja, H. Galina
Modyfikacja kompozycji epoksydowo-nowolakowej reaktywnymi kauczukami oraz napełniaczem węglowym.

Polimery 2006, 51 (11-12), 809-816.

**IF - 1.137, 27 points MNiSW, own contribution 85%**

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**H2.** **U. Szeluga**\*, L. Kurzeja, H. Galina
Curing of epoxy/novolac system modified with reactive liquid rubber and carbon filler.

Polymer Bulletin 2008, 60, 555-567.

**IF - 1.371, 25 points MNiSW, own contribution 85%**

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**H3.** **U. Szeluga**\*, L. Kurzeja, H. Galina
Dynamic mechanical properties of epoxy/novolac system modified with reactive liquid rubber and carbon filler.

Journal of Thermal Analysis and Calorimetry 2008, 92, 813-820.

**IF - 1.630, 27 points MNiSW, own contribution 85%**

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**H4.** **U. Szeluga**\*, P. Moryc
Curing of dicyanate ester/epoxy copolymers modified with polysiloxane and butadiene-acrylonitrile rubbers.

Journal of Thermal Analysis and Calorimetry 2012, 109, 73-80.

**IF - 1.982**, **25 points MNiSW, own contribution 85%**

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**H5.** **U. Szeluga**\*, P. Moryc
Viscoelastic properties and morphology of dicyanate ester/epoxy co-polymers modified with polysiloxane and butadiene-acrylonitrile rubbers.

Journal of Thermal Analysis and Calorimetry 2013, 14(1), 137-146.

**IF - 2.206**, **20 points MNiSW, own contribution 85%**

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**H6.** **U. Szeluga**\*, B. Kumanek, B. Trzebicka
Synergy in hybrid polymer/nanocarbon composites. A review.

Composites Part A: applied science and manufacturing 2015, 73, 204-231

**IF - 3.719**, **50 pkt. MNiSW, udział własny 65%**

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**H7.** S. Pusz, **U. Szeluga**\*, B. Nagel, S. Czajkowska, H. Galina, J. Strzezik
The influence of structural order of anthracite fillers on the curing behavior, morphology and dynamic mechanical thermal properties of epoxy composites.

Polymer Composites 2015, 36, 336–347.

**IF - 2.004**, **30 points MNiSW, own contribution 50%**

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**H8.** **U. Szeluga**\*, B. Kumanek, S. Pusz, S. Czajkowska

Preparation and characterization of carbon foams by carbonization of cyanate and cyanate/epoxy resins.

Journal of Thermal Analysis and Calorimetry 2015, 122 (1), 271-279.

**IF - 2.206**, **20 points MNiSW, own contribution 65%**

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**H9.** **U. Szeluga**\*, S. Pusz, B. Kumanek, K. Olszowska, S. Czajkowska, J. Myalski, J. Kubacki, B. Trzebicka, A.F. Borowski

Influence of unique structure of glassy carbon on morphology and properties of its epoxy-based binary composites and hybrid composites with carbon nanotubes.

Composites Science and Technology 2016, 134, 72-80.

**IF - 3.897**, **50 points MNiSW, own contribution 50%**

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**H10.** B. Kumanek, **U. Szeluga**\*, S. Pusz, A. Borowski, P. S. Wróbel, A. Bachmatiuk, J. Kubacki, M. Musioł, O. Maruzhenko, B. Trzebicka

Multi-layered graphenic structures as the effect of chemical modification of thermally treated anthracite.

Fullerenes, Nanotubes and Carbon Nanostructures, 2018, 26 (7), 405 - 416.

**IF 1.350, 15points MNiSW, own contribution 25%**

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**H11.** **U. Szeluga**\*, S. Pusz, B. Kumanek, J. Myalski, B. Hekner, B. Tsyntsarski, R. Oliwa, B. Trzebicka.

Carbon foam based on epoxy/novolac precursor as porous micro-filler of epoxy composites.

Composites Part A: applied science and manufacturing 2018, 105, 28-39.

**IF 4,017, 50 points MNiSW, own contribution 55%**

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**H12.** O. Maruzhenko Y. Mamunya, G. Boiteux, S. Pruvost, S. Pusz, **U. Szeluga**, B. Kumanek.

Influence of the carbon micro and nanofillers on the electrical and thermal properties of the segregated polymer composites. (w języku rosyjskim)

Polymer Journal 2017, 39 (4), 219-226.

**IF 0, 0 points MNiSW, own contribution 15%**

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_Impact Factor (IF) - odpowiedni do roku publikacji_

Publications reported as _scientific achievement_ are the equivalent of **339 points** according to the list of scientific journals of Ministry of Science and Higher Education (MNiSW) in Poland and have a **total IF 25.519** (by the year of publication, Web of Science).

**c) DISCUSSION OF THE SCIENTIFIC GOAL OF THE WORKS MENTIONED ABOVE AND THE RESULTS ACHIEVED TOGETHER WITH THE DISCUSSION OF THEIR POSSIBLE APPLICATION**

**I. INTRODUCTION AND RESEARCH OBJECTIVE**

**II. POLYMER MATRIX - CROSS-LINKING, PROPERTIES AND MODIFICATION**

**III. CARBON FILLERS - STRUCTURE AND PROPERTIES**

**IV. POLYMER - CARBON COMPOSITES**

**IV.1.** Composites with natural carbon fillers

**IV.2.** Composites with synthetic carbon fillers

**V. SUMMARY**

**I. INTRODUCTION AND RESEARCH OBJECTIVE**

Polymer composites are multifunctional and versatile materials that are currently used in almost all areas of life. These materials are implemented in innovative and advanced applications and construction materials that are useful in a variety of industries and modern technologies as well as in everyday activities. Composites are heterogeneous materials consisting of a polymer phase and dispersed types of other subsidiary substances, among which fillers deserve special attention. The phase with a continuous character is considered the matrix of the composite, whereas the filler is a dispersed or reinforcing phase that usually has a greater stiffness and mechanical strength than the polymer phase.

In the Polish-language specialist literature, the nomenclature for composites is not uniform. For composites in which particles of powdered filler form a more or less homogeneous dispersion, in addition to the "osnowa" designation, the term "matryca" [1-3] is often used as a direct translation of the English word "matrix". In the description of *scientific achievement*, I chose to consistently use the term "osnowa" because of its greater universality.

Properties of composites are determined by the characteristics and proportions of the individual components used to produce them, and the interactions between the polymer and other additives often contribute to the positive synergistic effect. The principal/fundamental role of the polymer matrix is to combine/associate all components of the composite into a whole. The properties greatly affect the thermal and mechanical properties of the composite as well as its resistance to chemical and atmospheric factors. The polymer matrix is responsible for transferring the stresses between the fillers and determines the processing method for the composite. The fillers applied to the polymer, both in continuous (fibers, fabrics) and powder form, modify practically all the physical properties of the resultant composites. The effect of the filler on the composite properties depends on its physicochemical characteristic, aspect ratio and the specifics of its particles distribution.

The properties of composites are determined by the mutual compatibility of individual components and the character of the interfacial interactions that affect the adhesion among the components. Powdered fillers are introduced into polymers to improve the mechanical, dielectric, thermal, chemical or processing properties (reduction of viscosity, shrinkage and exothermic effect of cross-linking).

The development and preparation of a new composite material with desirable parameters require a comprehensive study of the effects of the type and properties of the polymer matrix as well as the structure and properties of the filler on the composite parameters. Carbon materials are increasingly used as fillers. Despite numerous studies related to preparation and characterization of carbon-polymer composites, knowledge of the relationship between the carbon filler structure and the morphology and properties of the composite is still incomplete. This gap is a major obstacle to the efficient design of polymer-carbon composites with the desired properties.

For many years, the commonly used carbon fillers for polymers have been graphite and carbon black [4-9]. With the development of nanotechnology, interest has rapidly grown in polymer composites with nanofibers, carbon nanotubes [10] and, most recently, graphene [5,6]. The advantageous properties of carbon materials in combination with suitable polymers and modification possibilities using physical and chemical methods facilitate preparation of composites with improved mechanical strength and thermal resistance as well as good thermal and electrical conductivity.

The principal objective of this research, defined as the *scientific achievement* of the presented dissertation, was to determine the effect of the structure and properties of the polymer matrix and carbon materials on the morphology and properties of the composites obtained from these materials. One of the major problems that had to be addressed was determination of the relationship between the carbon filler-polymer interfacial interactions and the properties of the final composite materials.

Initial studies related to preparation and characterization of new carbon-polymer composites focused on the cross-linking process and properties of the cross-linked thermosets as potential matrices of the composites. The structure and physicochemical parameters of the carbon materials (naturally occurring and synthetic) used as micro- and nanofillers in the composites were examined in detail. Finally, polymer composites with new and previously non-used carbon fillers were prepared. The properties of the composites were studied, and the relationships between the structure of the carbon fillers and the morphology and properties of the composites were established.

Epoxy resin cross-linked with phenol formaldehyde resin or aliphatic amine and thermally cross-linked cyanate resin and its mixtures with epoxy resin were considered as polymer matrices. Cross-linked structures of this type have advantages such as a good thermal resistance, resistance to chemical and atmospheric conditions, dimensional stability, and low polymerization shrinkage, among others, but the disadvantages, i.e., fragility, low

fracture and resistance to crack propagation, significantly limit their application as a polymer phase in composites.

Improvement of the important mechanical parameters of polymer networks with high cross-linking density can be achieved with the addition of elastomeric modifiers. The results of these studies have been described in detail in publications **H1-H5**.

Both natural and synthetic carbon materials with different structures and properties have been used as powdered fillers in polymer composites. Carbon materials of natural origin with different degrees of organic matter metamorphism include bituminous coal **[H1-H3]**, anthracites of different order degree and graphite **[H7, H12]**. The use of two chemical functionalization processes on well-ordered anthracite produced two different graphene-based nanofillers **[H10]**. Two type of porous carbon materials, i.e., a carbon-foam type obtained from polymer precursors **[H8, H11]** and a glassy carbon - product of phenol-formaldehyde resin pyrolysis **[H9]**, were used as synthetic carbon fillers. Glass carbon was used alone as a filler in an epoxy matrix (binary composite) and in combination with carbon nanotubes as a secondary filler (hybrid composite).

Studies of carbon-polymer composites based on the mentioned polymer systems and the various carbon fillers determined the influence of the type of matrix and the carbon material on the morphology and properties of the composite materials. The influence of the structure, carbon content and presence of functional moieties in the carbon fillers on the course and the kinetic parameters of the cross-linking reactions of the polymer matrix were investigated **[H2**, **H7]**. The effects of carbon fillers on the properties of the final polymer-carbon composites (primarily viscoelastic, mechanical, electrical properties and thermal resistance **[H1**, **H3**, **H7**, **H9-H11]** and the molecular dynamics and activation energies of the transition processes **[H3]** were determined. The influence of well-ordered anthracite filler and processing methods on the properties of its composites with polyethylene and polypropylene was studied, and the results were described in publication **H12**.

The relationship between the morphology of composites with various carbon fillers, i.e., dispersion of the fillers in the polymer, adhesion and the character of the polymer-carbon interfacial boundaries on the properties of the obtained materials, was also investigated **[H1**, **H3**, **H7**-**H12]**.

The detailed research results presented below in the description of *scientific achievement* are divided into sections for clarity. The analysis of the polymer matrices (chapter 2), the production and characterization of the applied carbon fillers (chapter 3) and the morphology and properties of the final polymer-carbon composites (chapter 4) are discussed separately.


## II. POLYMER MATRIX - CROSS-LINKING, PROPERTIES AND MODIFICATION [H1-H5]

The high thermal resistance, which reaches practically up to 450 °C, of cross-linked epoxy resins and cyanate esters combined with high mechanical strength prevents their use in

many areas, especially as construction materials and the molding compounds. The addition of fillers improves the mechanical and thermal properties and the thermal and electrical conductivities of composites based on these polymer systems. However, significant fragility, low fracture resistance and susceptibility to the crack propagation due to the high cross-linking density of thermosetting systems motivate the search for methods to improve these parameters.

Studies of the cross-linking reactions and properties of the polymeric systems presented in publications **H1-H5** optimized the process conditions and improved the final properties of the cross-linked epoxy and cyanate matrices. In addition, to improve the processing and mechanical properties, these resins were modified with acrylonitrile-butadiene rubbers terminated with reactive carboxyl (CTBN) or epoxy (ETBN) groups. The effect of rubber domains precipitated in a chemically induced phase separation process on the kinetic parameters of the cross-linking of epoxy resin and cyanate ester and its mixtures with epoxy resin were determined. The viscoelastic properties and mechanical strength of two-phase epoxy systems modified with rubbery agents were studied compared with those of a pristine polymer matrix. Observations of the influence of the polysiloxane core-shell modifier on the cross-linking and impact strength of cyanate resin and its mixtures with an epoxy resin were also performed.

The aim of the study in **H1** was to determine the effect of CTBN and ETBN rubbers on the morphology and mechanical properties of an epoxy matrix obtained by cross-linking of a diglycidyl ether of bisphenol A (EP) with a phenol-formaldehyde resin (novolac type, NZ). Microscopic observations (Fig. 1) revealed a close relationship between the character of the interfacial boundary between the spherical domains of CTBN or ETBN and the epoxy resin and the mechanism of deformation during mechanical damage.
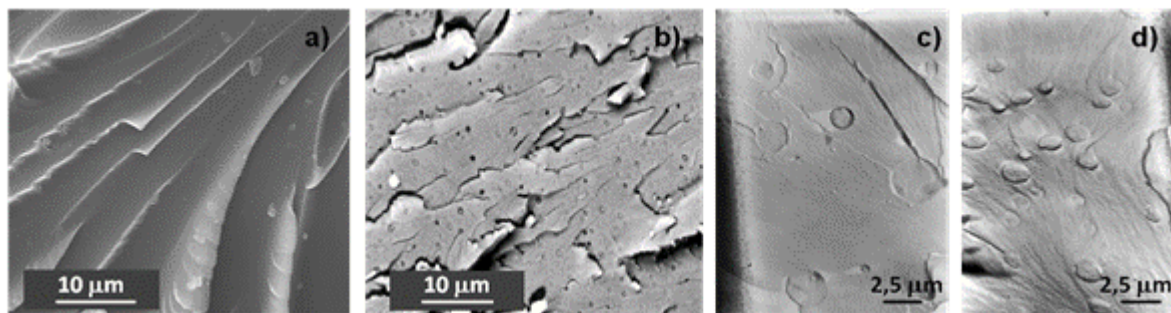


**Fig. 1.** Micro-photographs: a) SEM pristine epoxy matrix, b) SEM composite with 6 mass% ETBN, c) TEM composite with 6 mass% CTBN, d) TEM composite with 6 mass% ETBN.

The rubber particles significantly affected the morphology of the brittle fracture surface of the epoxy matrix. The CTBN and ETBN particles were strongly bound to the epoxy continuous phase (Figure 1b, d), and the plastic shear bands formed in the areas between the rubber particles contributed to increased mechanical strength. The rubbery domains exhibited good adhesion to the surrounding epoxy resin and acted as concentrators for crack initiation and propagation during polymer system damage. Additionally, the plastic deformation bands in

the modified polymer matrix contributed to increased energy absorption and a more pronounced increase in the fracture resistance and mechanical strength.

The effect of CTBN and ETBN content of up to 16 mass% on the storage modulus (E') and glass transition temperature ($T_g$) of the epoxy matrix were studied using dynamic mechanical analysis (DMA). It was found that the cross-linking density of the epoxy network decreased for all systems modified with CTBN and ETBN rubber, resulting in a decrease of the storage modulus, particularly in the rubber-like region. According to the theory of elasticity for polymers, the E' value after glass transition is directly related to the average molecular weight of the chains between the network junctions. The more flexible epoxy-novolac structure containing 9 mass% was characterized by a flexural mechanical strength that was improved by nearly 70% compared with pure epoxy matrix. The effects of the rubber end groups and modifier content on the impact strength and fracture energy were determined as described in the Appendix chapter in **H2**. The results confirmed that ETBN-modified systems demonstrated up to 150% improved impact strength relative to the pure epoxy matrix. Additionally, 6 mass% of rubber introduced into the epoxy resin was the optimal amount needed to achieve a more flexible epoxy network and increased fracture toughness and flexural strength without a decrease in $T_g$ compared with the pure epoxy matrix. From a practical point of view, increasing the flexibility of the matrix greatly facilitates processing of subsequent composites with fillers and other additives.

The aim of the investigation of the cross-linking reactions in epoxy resin with the phenol-formaldehyde resin described in **H2** was to determine the influence of CTBN and ETBN rubbers on the process kinetic parameters because cross-linking of epoxy resins with hydroxyl compounds is known to be a complex process [11-14]. The use of additional components (e.g., another polymer or filler) to improve the essential properties of composites, such as impact resistance, can completely change the cross-linking process [15-17].

The epoxy resin conversion in the presence of ETBN or CTBN and the associated kinetic parameters were determined based on the reaction heat changes measured under both isothermal and non-isothermal conditions using differential scanning calorimetry (DSC). Two primary reactions occur in a mixture of epoxy resin and novolac resin: (1) epoxy ring opening by the hydroxyl group in the phenol-formaldehyde resin and (2) formation of an insoluble polymer by reaction of the product of the first reaction with the next oxirane ring. The presence of a single exothermic peak regardless of the cross-linking conditions confirmed that these two reactions occur simultaneously. Changes in the conversion and reaction rates indicated that the epoxy resin cross-linking reactions with novolac proceeded in autocatalytic manner and also in the presence of CTBN or ETBN rubber.

The reaction coefficients and the reaction order in isothermal conditions were designated from the general Kamal equation proposed for reactions of epoxy resin with amines [11-13]. This equation considers the catalytic effect of the hydroxyl groups formed during the cross-linking reaction of the epoxy resin and those present in the studied system.

Another area of study investigated the influence of the rubber phase separation that occurs during cross-linking of the epoxy resin on the kinetic parameters of this process. Analysis of the reaction rate as a function of time under isothermal conditions confirmed that the separation process in both rubbers did not change the mechanism of epoxy network formation but caused a certain shift in the maximum of the reaction rate curve towards lower temperatures. Acceleration of the cross-linking reaction at its initial stage by the hydroxyl groups of CTBN rubber (growth in reaction rate coefficient) was an effect of the hydrogen bonds formed with the oxygen from the epoxy groups. It is well known [14] that weakening of the C-O bond in the ring makes it easier to break. At a later stage, the precipitated CTBN acted inversely to reduce the reaction rate coefficient, and the effect of ETBN on the rate coefficient at the first stage of cross-linking was negligible. In the next step, an increase of the rate coefficient similar to that observed for the CTBN-modified epoxy system was noted due to phase separation of ETBN.

The lower activation energy of the reaction in the presence of CTBN, as determined from the Arrhenius temperature dependence of the reaction rate coefficients [18], confirmed the catalytic effect of this rubber on the cross-linking of epoxy resin. The activation energy of the cross-linking of the ETBN-modified epoxy resin was unaffected and was comparable to that of the unmodified system. The analogous effect of CTBN and ETBN rubbers on the activation energy of the epoxy resin cross-linking reactions with the novolac resin as determined, by the non-isothermal Kissinger [19] and Flynn-Wall-Ozawa [20] methods, was observed relative to that predicted by Arrhenius dependence.

The effects of the CTBN and ETBN rubbers on the reaction heat and kinetic parameters of the cross-linking reactions of epoxy resin are important for processing of modified epoxy systems.

The work in **H3** adapted the preparation method for the modified epoxy systems from **H1** and **H2**, and the effects of the CTBN and ETBN rubber content on the viscoelastic properties (i.e., storage modulus, loss modulus (E") and loss factor (tan $\delta$)) of the cross-linked EP/NZ networks in their $\beta$- and $\alpha$-transition regions were determined.

The decrease in the storage modulus for both the glassy and rubbery-like states based on the CTBN and ETBN rubber content confirmed that the cross-linked epoxy-novolac system modified with these rubbers was characterized by greater flexibility manifested in a lower stiffness and resistance to bending deformation. The increase in the width and decrease in the intensity of the E" and tan $\delta$ peaks proved that the rubber domains influenced the glass transition of the epoxy network. The increase in the rubber content caused a reduction in $T_g$ and an broadening of the transition temperature range, indicating the increased flexibility and heterogeneity of the structure.

A study of the viscoelastic properties as a function of frequency was performed based on the assumptions of the time-temperature superposition (TTS) theory, which predicts that the process of the molecular transition in polymer materials occurs more rapidly at elevated temperatures and that an equivalence between the time (frequency) and temperature exists. Characterization of the transition processes related to molecular

motions in the epoxy systems was focused on determination of the CTBN and ETBN effect on the activation energy of $\beta$- and $\alpha$-molecular transitions. The activation energy of $\beta$-transition related to motions of the side chains and end groups was determined using the Arrhenius model [20]. The CTBN and ETBN rubbers caused a reduction of the activation energy of $\beta$-transition in the modified epoxy systems.

The Wiliams-Landel-Ferry (WLF) model [21] was used to determine the activation energy of the glass transition, which drastically changes the dynamics of overall system and does not satisfy the Arrhenius relationship. In the glass transition region for cross-linked epoxy systems, the isothermal curves for the storage and loss modulus were shifted to the reference temperature ($T_g$), producing the reduced curves or so-called "master curves" over a wide frequency range.

The dependence of the loss modulus on temperature at different oscillation frequencies and the reduced loss modulus curve for an epoxy system modified with CTBN rubber are shown in Fig. 2.
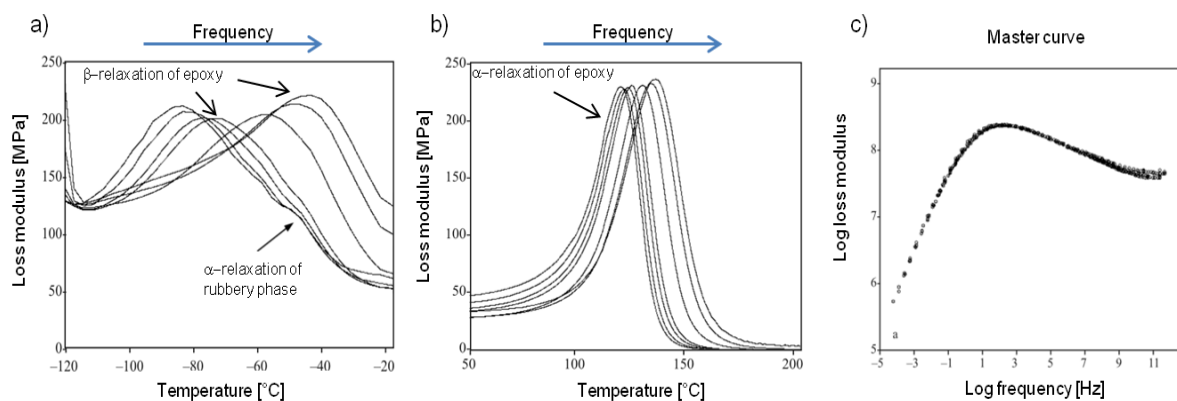


**Fig. 2**. Loss modulus as a function of temperature for different frequencies: a) low temperature, b) higher temperature and c) "master curve" for epoxy system with 6 mass% CTBN.

The reduced curve (Fig. 2c) constructed using the superposition principle confirmed that it is possible to transform the viscoelastic properties into a wider frequency (time) range. Shift factors determined during construction of "master curve" were used to calculate the activation energy of $\alpha$-transition for EP/NZ systems modified with CTBN and ETBN and were compared with those of the neat epoxy matrix.

It was found that addition of CTBN and ETBN contributed to the increase in the activation energy of the main chain movements in the region of the glass transition compared with that of the neat epoxy matrix. The increase in $\alpha$-transition activation energy was due to the spatial hindrance caused by the presence of the rubber domains in the continuous epoxy phase.

Study of the frequency-dependent viscoelastic properties, the activation energy of molecular transitions for polymer matrices, and the effect of additional substances, including elastomeric modifiers, is highly important from the point of view of their long-term use in variable load conditions.

Other polymer systems studied due to their promising thermomechanical properties included cyanate ester and its mixture with an epoxy resin (**H4** and **H5**). Cyanate ester (CE, aryl ester of cyanate acid) thermally cross-linked in the presence of a catalyst (copper II acetylacetonate) formed a polycyanurate structure. The reactions of the CE resin with various amounts of epoxy resin (EP) resulted in cross-linked cyanate-epoxy systems (CE/EP) composed of oxazolidone, isocyanurate and polyether structures.

The cross-linking processes of the cyanate ester and its mixtures with an epoxy resin are known and have been described in the literature [22]. The schemes of the possible reactions involving cyanate and epoxide compounds are shown in Fig. 3.
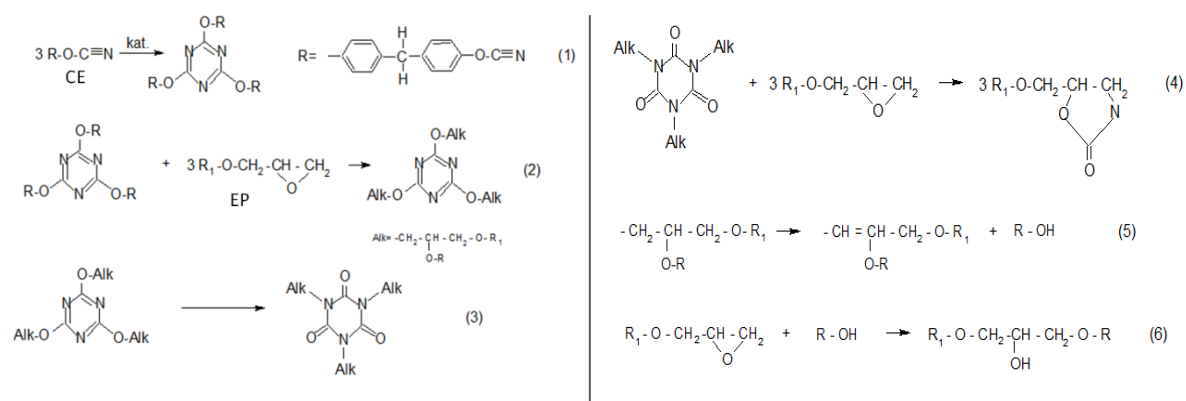


**Fig. 3.** Scheme of cross-linking reactions in CE and CE/EP systems [22].

Investigations of the cross-linking process for cyanate ester and its mixtures with epoxy resin were performed via the DSC method. The effect of the epoxy monomer content on the course of the cyanate ester cross-linking reactions was also studied. The changes in heat flow with temperature, as shown in Fig. 4, confirmed the effect of dilution by epoxy resin on the cross-linking process of the cyanate ester.
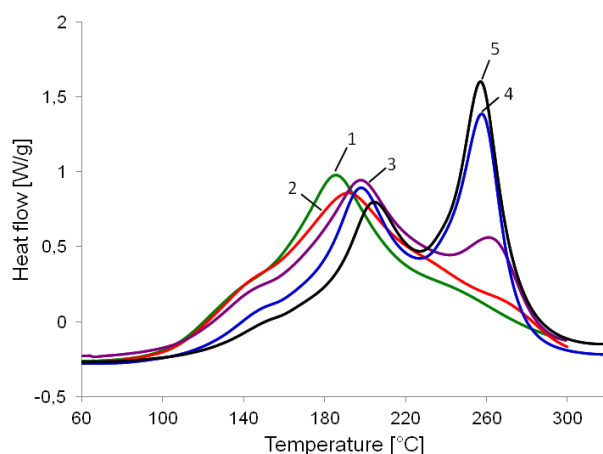


**Fig. 4.** Heat flow as a function of temperature for: (1) CE, (2) CE/EP (90/10), (3) CE/EP (80/20), (4) CE/EP (60/40), (5) CE/EP (30/70) (DSC, heating rate 10 °C/min).

Analysis of the thermograms for CE/EP systems with different contents of epoxy monomer allowed assignment of the individual reaction stages of epoxy groups with the triazine ring and with the cyanate monomer (according to Fig. 3) to the observed thermal effects.

The first peak on the thermogram of the cross-linking CE without addition of EP is related to the reaction of triazine ring formation (Fig. 3, reaction 1). During cross-linking of the CE/EP mixtures in the temperature range of this peak, the products of the epoxy group reaction with the triazine ring were obtained (Fig. 3, reaction 2). The second peak observed for the CE/EP mixtures was a consequence of the isomerization reaction of the triazine ring to the isocyanurate ring and further reactions with the epoxy groups, including post-crosslinking reactions of the epoxy structures (Fig. 4, reactions 3-6). A number of intermediates (oxazoline, oxazolidone, isocyanurate and polyether structures) were formed depending on the content of the epoxy resin.

The intensity of the trimerization peak (formation of triazine rings) decreased with increasing epoxy resin content, and its maximum moved towards higher temperature. At the same time, the intensity and area of the second peak associated with reactions involving epoxy groups, i.e., isomerization of triazine rings to isocyanurate rings, was observed to increase followed by their cleavage and the formation of oxazolines.

Investigations of the cross-linking reactions showed that use of epoxy resin to modify the cyanate ester produced mixed structures with lower cross-linking density. This result was directly due to the presence of oxazoline or polyether structures, in contrast to the densely cross-linked network of the unmodified cyanate ester composed exclusively of triazine rings. Fracture tests on cross-linked cyanate-epoxy systems showed that addition of epoxy resin had a positive effect on the impact strength, and a 20% increase was observed for 30 mass% of epoxy resin in the mixture. A further increase in the epoxy resin content resulted in increased impact strength at the expense of $T_g$ and thermal resistance.

For additional improvement in impact resistance, pure CE and EP/EP (70/30) mixtures were modified with ETBN rubber and a polysiloxane core-shell modifier. The polysiloxane powder particles formed a homogeneous dispersion, and their presence did not change the course of the cross-linking reactions, contributing to a 55% increase in the impact strength of the CE resin. The use of ETBN was less effective, and the impact strength improvement for both systems was lower than for polysiloxane. Furthermore, the increase in impact resistance and mechanical strength for CE and ETBN-modified CE/EP systems was significantly lower than the 150% improvement in impact strength for epoxy-novolac [H2]. The reason for the poor modification effects was the higher cross-link density of the polycyanuranate network and the stiffness of chains between the cross links in the CE network compared with those of EP/NZ.

The viscoelastic properties of cross-linked CE and CE/EP systems with different contents of epoxy resin investigated by the DMA method were discussed in **H5**. Materials cross-linked under different temperature conditions, i.e., (1) at 180 °C, (2) at 180 °C and subsequently at 220 °C were characterized. The neat cyanate and epoxy/cyanate co-polymer (30/70) were additionally cured at 180 °C, then at 220 °C and post-cured at 250 °C to check the influence of

temperature conditions on the $T_g$. It was found that further cross-linking at temperatures greater than 200 °C was necessary to obtain a fully cross-linked CE or CE/EP network.
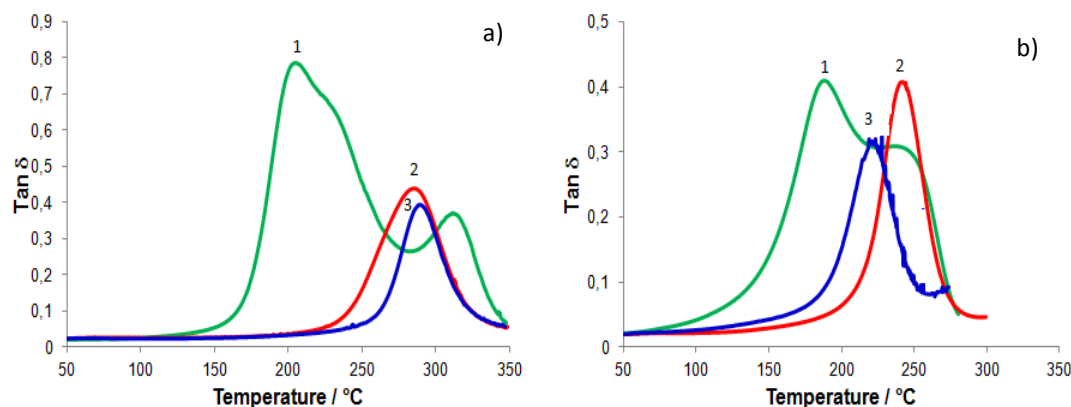


**Fig. 5.** Effect of cross-linking temperature on tan δ for: a) CE, b) CE/EP (70/30)
Curve 1) 180 °C, curve 2) 180 °C and subsequent 220 °C, curve 3) 180 °C, subsequent 220 °C and 250 °C.

Two peaks found in the tan δ temperature dependences (Fig. 5a and 5b, curve 1) indicated inhomogeneities in the CE and CE/EP polymer networks obtained at 180 °C. An increase in structure homogeneity and an increase in $T_g$ for cyanate resin without epoxy resin was obtained by cross-linking at both 220 and 250 °C (Fig. 5a, curve 2 and 3). In the case of CE/EP, cross-linking at 250 °C (Fig. 5b, curve 3) resulted in $T_g$ reduction, whereas a favorable increase in $T_g$ for this system was obtained at 220 °C (Fig. 5b, curve 2). It was found that all CE/EP systems were characterized by a lower $T_g$ due to their lower cross-link density compared with that of CE. The higher flexibility between the cross-links in the CE/EP network due to higher molecular weight was confirmed by a gradual reduction of the storage modulus with an increase in the epoxy resin content. Differences in the viscoelastic properties of the CE and CE/EP systems resulted from a different structure of fragments between the cross-links in their networks. The presence of rigid and symmetric chains composed of triazine rings directly affected the high storage modulus and $T_g$. Replacement of the triazine rings in the cross-linked CE/EP systems by oxazoline and oxazolidone rings led to structures with lower stiffness and thermal resistance with increasing amounts of epoxy resin.

The DMA studies of CE/EP systems clearly proved that notably small structural changes caused by excessively high cross-linking temperature (250 °C) led to significant reductions in $T_g$, whereas thermogravimetric analysis showed only a slight mass loss up to 400 °C. The temperature of maximum decomposition rate for CE/EP systems decreased as the epoxy resin content increased. The smallest mass loss at 800 °C (below 50% of initial mass) was observed for CE.

Publication **H5** showed that modification of CE and CE/EP systems with butadiene-acrylonitrile rubber functionalized with epoxy groups and a polysiloxane core-shell modifier led to final polymer materials with improved properties and produced a good compromise between mechanical and thermal properties.

## III. CARBON FILLERS - STRUCTURE AND PROPERTIES [H1- H3, H7-H12]

Determination of the effect of carbon fillers on the morphology and properties of the obtained polymer-carbon composites required detailed characterization of these materials in terms of their structure, presence of functional groups and physicochemical properties. Naturally occurring and synthetically produced carbon materials were applied in the role of micro- and nanofillers for polymer composites.

In **H1-H3**, bituminous coal from the Bielszowice mine with a medium metamorphism degree was used as a filler in epoxy resin cross-linked with novolac resin. The content of element C was approximately 84 mass%, and a significant amount of oxygen (approx. 10 mass%), present mainly in the form of functional groups, was found in the structure of this carbon matter. In addition to more or less condensed aromatic structures, this carbon material also contained heterocyclic rings with oxygen and nitrogen atoms and reactive moieties, mainly hydroxyl, carbonyl, carboxyl, and amine. The thermally treated coal underwent both recondensation and decomposition processes. Mass loss was observed from 400 °C associated with the release of aliphatic and alicyclic moieties present in the carbon structure in the form of volatile degradation products.

Filler particles obtained by grinding the coal to a fraction below 80 μm took the form of isometric, irregular grains and were directly dispersed in the polymer medium after removal of moisture. Compared with typical mineral or metallic fillers, the poorly developed specific surface (5.5 m$^2$/g), low density (1.3574 g/cm$^3$), and the high thermal stability make these materials a promising and inexpensive filler for polymer composites.

Another group of natural carbon materials used as fillers for polymer composites **[H7, H10, H12]** were anthracites characterized by the highest metamorphism of carbon matter, with a C content of up to 98 mass%. The smaller number of functional groups attached to the carbon skeleton makes the anthracite a more inert component of polymer-carbon composites compared with bituminous coals. In contrast to other coals, anthracites were also characterized by a significant degree of ordering of the basic structural units (graphene sheets). The susceptibility of the anthracite structure to structural transformation under thermal treatment, from a poorly ordered turbostratic structure to a well-ordered graphite-like structure [25-27], offers the possibility of using anthracite as a precursor of layered carbon fillers.

The study in **H7** described the use of anthracite to preparation of layered well-ordered carbon fillers. The initial material, anthracite Swierdlowski (SVraw, Donbas, Ukraine), was characterized by a simple petrographic composition and high structural homogeneity. It was found that pyrolysis of the anthracite precursor at 2000 °C caused structural transformation (Fig. 6), from the initial turbostratic structure (SVraw) to a graphite-like structure (SV2000) associated with an increase in the graphene sheet order and in carbon content, from approx. 91 to 98 mass%. These changes were accompanied by an increase in the true density of the carbon matrix.

Structural and chemical changes occurring in anthracite as a result of the pyrolysis process were investigated via optical microscopy (OM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and FT-IR and Raman spectroscopy. All these methods confirmed significant differences in the structure of both anthracites. It was found that the raw anthracite particles had an isometric shape with a poorly visible layered structure (Fig. 6a), whereas the grains of SV2000 anthracite consisted of multilayered aggregates (Fig. 6b) with a structure similar to that of graphite (Fig. 6c).
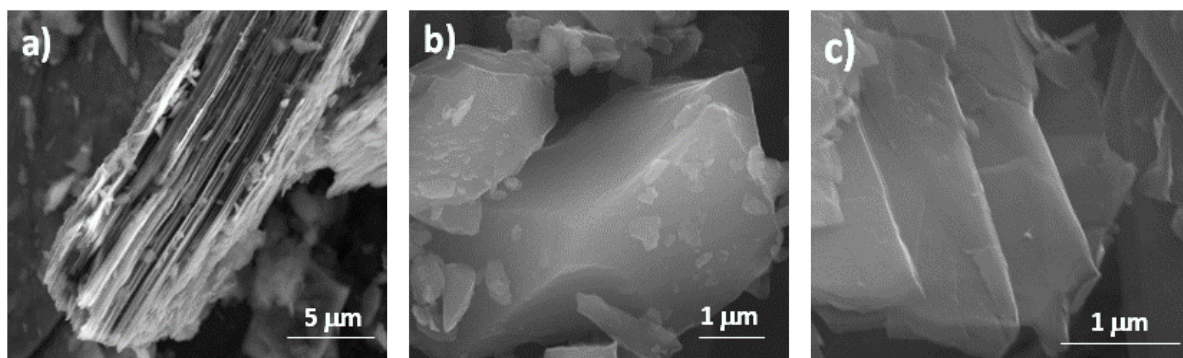


**Fig. 6**. SEM microphotographs (a) SVraw, (b) SV2000 and (c) natural graphite.

The reflectance parameters, XRD analysis, and Raman spectroscopy results confirmed significant differences in the structure of both anthracites. Thermal treatment of SVraw anthracite resulted in an increase of the XY dimensions of the graphene layers and the height of stacks in which they were arranged, whereas the interlayer spaces were decreased. All these parameters corresponded to the characteristic values of graphite [25-27].

The Raman spectrum of SV2000 showed a significant change in the intensity and the width of the D- G- and 2D-bands characteristic of carbon materials [28,29] compared with those of SVraw (Fig. 7).
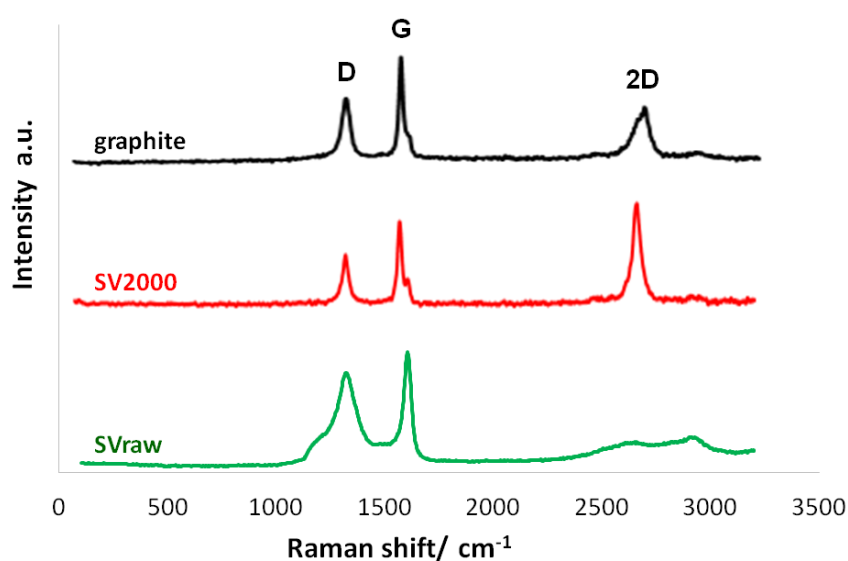


**Fig. 7.** Comparison of Raman spectra for anthracites of various order degree and graphite **[H7]**.

The ratio of the intensity of D (~1359 cm$^{-1}$) associated with disordered sp$^3$ hybridization and G-band (~1600 cm$^{-1}$) corresponded to a polyaromatic graphite structures (C-sp$^2$) with a change from 0.82 for SV raw to 0.62 for SV 2000, thus confirming the increase in structure ordering and decrease in defect number in the graphene sheets after heat treatment of anthracite. Based on the FTIR study, it was found that the most oxygen functional groups (hydroxyl, carboxyl, ether, etc.) present in the initial anthracite were eliminated during pyrolysis. As expected, changes were observed in the material properties of anthracite with increasing order of its structure.

These studies showed that the initial anthracite had a turbostratic structure composed of small stacks of graphene layers arranged locally and also containing alkyl chains, aliphatic groups and moieties involving heteroatoms. Pyrolysis of the anthracite at 2000 °C contributed to transformation of its poorly ordered structure into a graphite-like structure composed of graphene sheets that formed higher stacks arranged in one preferential direction.

**H12** describes the use of well-ordered anthracite SV2000 as a filler of so-called segregated composites based on thermoplastic matrices (polyethylene, polypropylene). The dispersion of the filler was prepared by mechanical mixing the anthracite powder with the thermoplastic granules in the mortar leading to the formation of the shell layer of carbon filler on surface of the polymer particles due to electrostatic interactions. Grains of plastic coated with anthracite powder were processed using hot compacting method. Additionally, the dispersion with random distribution of conductive anthracite particles in thermoplastics were prepared using screw extruders The improving of electrical conductivity of composites as a result of segregated (ordered) distribution of anthracite particles creating a network of conducting paths in polymer led to essential increase of electromagnetic interference shielding efficiency owing to multiple reflection of electromagnetic waves on the walls of carbon framework. The segregated composites were characterized by the threshold of percolation of electrical properties 2.95% vol. anthracite compared to the content of ~ 25% vol. anthracite for the composite in which the dispersion of the filler in thermoplastics was obtained in screw extruders.

Anthracite SV2000 was subjected to the functionalization process described in **H10**. Chemical functionalization of SV2000 was performed using two different methods. The main purpose of the work in **H10** was to demonstrate that the graphite-like anthracite is a suitable precursor for obtaining multi-layered graphenic fillers with functional groups that increase their compatibility with polymers. The scheme of the functionalization of anthracite material is shown in Fig. 8. The first method was based on oxidation of anthracite by the modified Hummers method [30]. The resulting anthracite oxide (SV2000-GO) was subjected to an expansion process at 900 °C followed by thermal reduction of the oxygen functional groups attached during oxidation (Fig. 8a). As a result, a reduced anthracite oxide (SV2000-rGO) with increased interlayer distances, and well-separated carbon sheets were obtained (Fig. 8b).
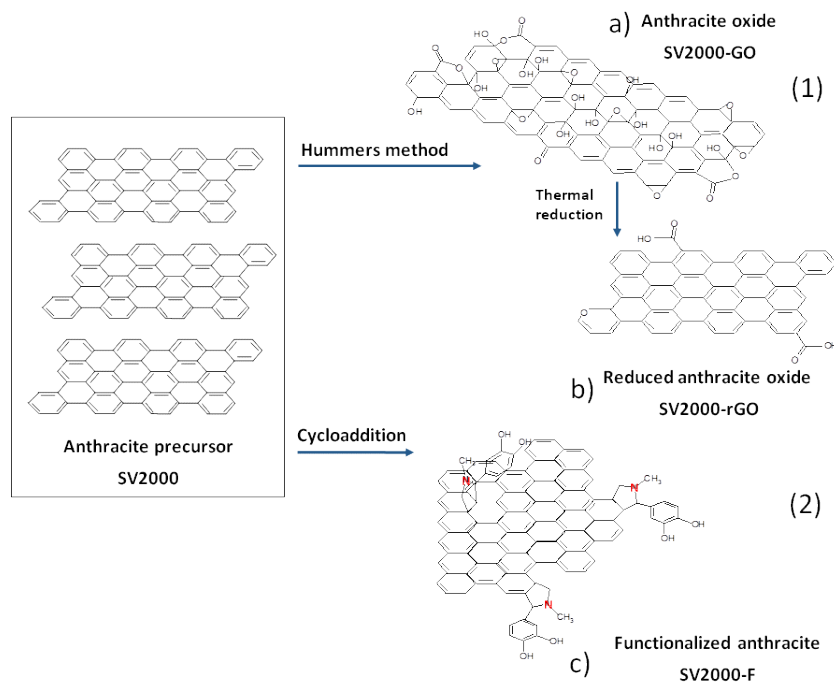
**Fig. 8**. Scheme of chemical procedures used to obtain graphenic materials from SV anthracite precursor: (1) Hummers method with thermal reduction, (2) cycloaddition of azomethine ylide.

The second method of functionalization consisted of 1,3-dipolar cycloaddition of the azomethine ylide obtained in reaction of N-methylglycine with 3,4-dihydroxybenzaldehyde to the $sp^2$ carbon bonds of graphene sheets of anthracite after exfoliation in pyridine (Fig. 8c), according to the procedure proposed for graphite [31]. The strong polar solvent, i.e., pyridine, was used to weaken and destroy the transverse hydrogen bonds in the anthracite structure and consequently to assist in separation of the graphene layers by ultrasonic treatment and increase their susceptibility to functionalization.

The results of microscopy (TEM, SEM, AFM) and spectroscopic studies (Raman, FTIR, XPS) showed that the structures of the graphenic materials obtained by (1) functionalization of anthracite through oxidation followed by thermal reduction and (2) cycloaddition of dienophile were significantly different.

As confirmed by the Raman spectroscopy, both methods led to a decrease in the structure order and an increase in the number of defects in the graphene sheets with reference to the initial SV2000 precursor. The greatest disturbance of the structure was observed for anthracite oxide, as reflected in the increase in the area of the D-peak associated with the presence of sp3 carbon. Thermal reduction of this oxidized form combined with expansion of the graphene sheets caused reordering of the structure (reduction in the D-peak intensity).

The TEM observations revealed differences in the carbon layer ordering for the obtained graphenic materials (Fig. 9). The graphite-like structure of the initial SV2000 (Fig. 9a) was substantially reproduced in SV2000-rGO (Fig. 9b), whereas in anthracite functionalized by ylide cycloaddition, this well-ordered structure was strongly disturbed (Figure 8c).
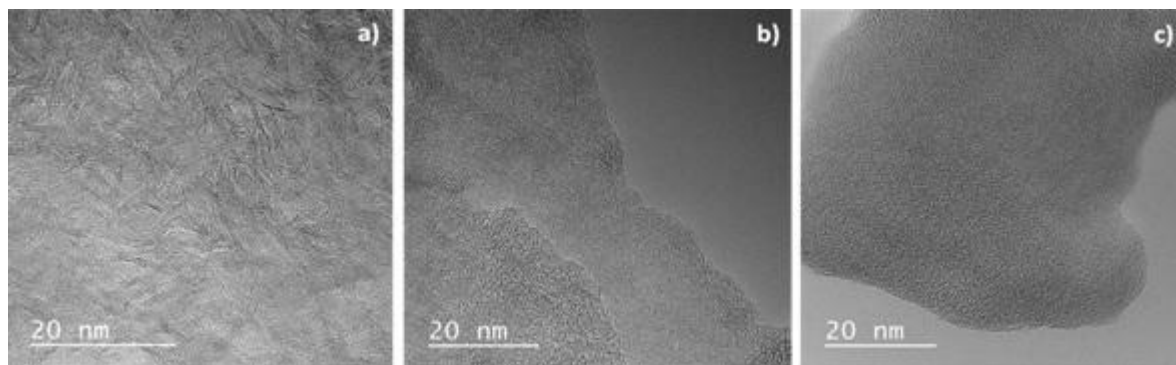
**Fig. 9.** TEM microphotographs: (a) anthracite SV2000, (b) thermally reduced anthracite oxide (Hummers method), (c) anthracite functionalized by ylide cycloaddition.

The increase in the number of defects in the SV2000 graphene structures was due to attachment of functional groups such as hydroxyl, carboxy, carbonyl, ether, epoxy, etc., as confirmed by detailed analysis of the FT-IR spectra and C1s, O1s and the N1s core lines obtained via X-ray photoelectron spectroscopy (XPS, Fig. 10a). The thermal reduction led to the elimination of a portion of these groups (Fig. 10b).
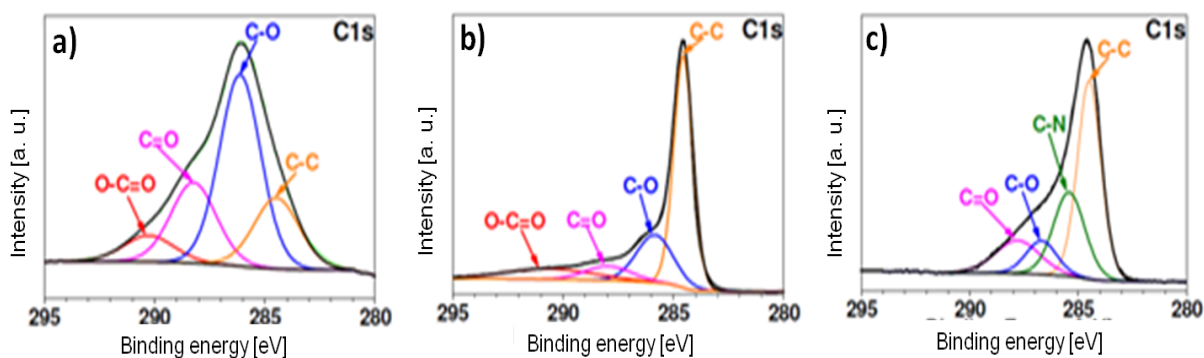


**Fig. 10.** XPS spectroscopy and C1s core lines: a) SV2000-GO, b) SV-2000-rGO, c) SV2000-F.

A notably large contribution of oxygen and nitrogen-containing methyl-2-(3,4-dihydroxyphenyl)pyrrolidine groups 3,4-bonded to the graphene sheets (Fig. 10c) was observed for material functionalized by cycloaddition of ylide to SV2000 anthracite.

Using SEM and AFM microscopy, it was found that SV2000-rGO contained well-separated graphene layers. The flakes of this anthracite material were 6-30 nm thick and corresponded to commercially available multi-layered graphene nanoplatelets. In turn, functionalization of anthracite by azomethine ylide cycloaddition led to the formation of graphenic material in the form of nanoflakes with considerably smaller XY dimensions (<200 nm) and thickness (1-3 nm).

The resulting layered graphene materials were subsequently used as well-defined carbon nanofillers in polymer composites (Chapter 4.1).

Another group of carbon materials with a completely different structure and properties proposed as carbon fillers in polymer composites was carbon foams obtained from polymer precursors. The work in **H8** investigates the preparation of light carbon materials with a high porosity (> 90%) by carbonization of thermoset polymers. Cross-linked cyanate ester

of bisphenol A and its systems with 20 and 40 mass% of diglycidyl ether of bisphenol A were prepared according to the procedure described in **H5** and applied as polymer precursors of carbon foams. Carbonization of cross-linked polymer systems was performed under nitrogen at 500, 600 and 900 °C with a heating rate of 3 °C/min.

The morphology and properties of the final products confirmed that porous carbon materials with a pore size of 50-200 μm, a density less than 0.4 g/cm$^3$ and a high carbon content could be directly prepared by carbonization of the polymer matrix at ambient pressure without the use of additional foaming agents.

Comparison of FTIR data for the polymer precursors and the carbon foams produced from them supplied a wealth of information on the effect of temperature on the chemical structure of porous carbon materials. The bands characteristic for the triazine, epoxy, and methyl functional groups disappeared, and above 900 °C, only the absorption bands characteristic for the carbon skeleton were observed.

The porous structure of the carbon foams was created due to the self-foaming ability of the cross-linked cyanate and cyanate/epoxy systems at sufficiently high temperature by products of their thermal decomposition. The release of small fragments of the polymer network and low-molecular volatiles led to the formation of a carbon skeleton with a high true density (~2 g/cm$^3$). The carbon content increased with the carbonization temperature, and at 900 °C, it was finally possible to reach 91% C.

It has been shown that in the first stage, thermal degradation of the cross-linked cyanate and its systems with epoxy resin was related to the decomposition of C-O-C ether bonds between the phenyl rings and triazine or epoxy rings characterized by the lowest energy. The low-energy process of bond breaking in the polymer network led to a highly porous structure without micro-damage or micro-cracking.

SEM photographs (Fig. 11) showed similar morphologies for the carbon foams derived from the selected precursors and carbonized under the same temperature conditions.
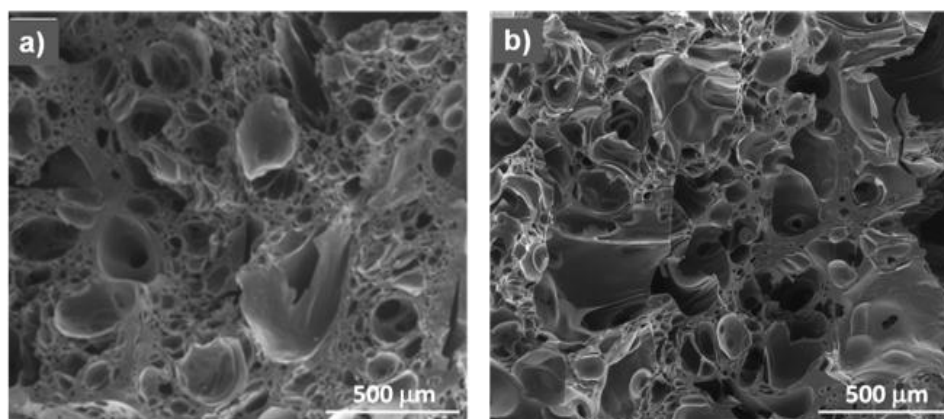


**Fig. 11.** SEM microphotographs of carbon foams obtained at 900 °C from: (a) CE and (b) CE/EP precursors.

As expected, the thermal stability of the carbon foams increased gradually with carbonization temperature due to the increasing content of C in the carbonizates. Porous

carbon materials obtained from a CE/EP precursor (80/20) exhibited a temperature for the maximum rate of mass loss that was approximately 50 °C higher than that of carbon foam from the CE precursor. The most thermally stable carbon foam was obtained using the CE/EP (80/20) precursor at 900 °C and showed only 2.7% mass loss at 800 °C. The resulting porous materials were electrically conductive and had advantageous mechanical properties such as Young's modulus and compression strength.

**H8** directly contributed to the development of an easy and repeatable methodology for obtaining carbon foams with good physical properties that retained their specific structure even after crushing to a particle size of less than 300 μm (SEM examination), which offers the possibility of their use as a filler for polymer composites.

Another carbon material considered as an interesting filler for polymer composites was the glassy carbon (GC) described in **H9**. Glassy carbon is a synthetic carbon material with a significant content of C (greater than 90 mass%) and a lower total porosity than the carbon foams. This material was obtained for the first time in the 1970s from phenolic resin [32]. The structure of glassy carbon has not yet been clearly determined, and several structural models exist in the literature.

The first hypothesis proposed by Nody and Inagaki [33] assumes that glassy carbon is composed of trigonal carbon atoms ($sp^2$) that form two-dimensional graphite-like small domains and tetrahedral domains ($sp^3$) (Fig. 12 a1) linked by different types of bonds. Typically, as the heat treatment temperatures increased, the trigonal carbon atom content increased, and at the same time, the content of the tetrahedral carbon atoms decreased significantly in the glassy carbon structure.

Jenkins and Kawamura [34] presented a glassy carbon structure consisting of ribbon-like graphitic domains of $sp^2$-hybridized carbon atoms stacked in layers (microfibrils) that were irregularly twisted and entangled (Fig. 12 a2).
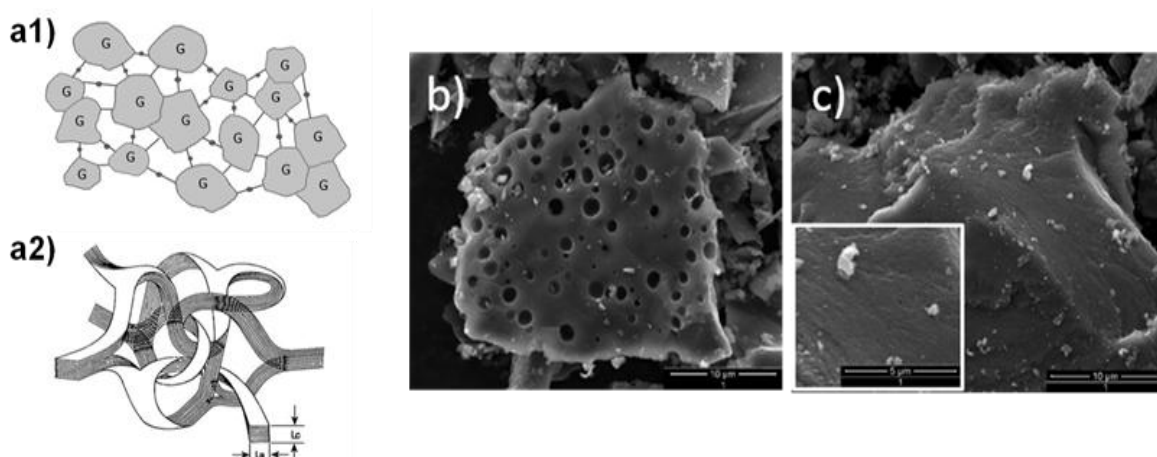


**Fig. 12**. Structural models of glassy carbon: Nody and Inagaki [33] (a1), Jenkinsa and Kawamury [34] (a2) and own SEM microphotographs of glassy carbon grains (b, c).

The glassy carbon studied in **H9** was produced from a resole type of phenol-formaldehyde resin through slow pyrolysis to 1000 °C with a heating rate of approximately 30 °C/h. The

low heating rate was particularly important in the thermal degradation temperature range of the polymer networks (370-620 °C), leading to a porous carbon skeleton (Fig. 10b, c). The slow temperature increase produced a proper structure of the product. After pyrolysis, the glassy carbon contained 92 mass% carbon and 6.9 mass% oxygen. The true density was 1.45 g/cm$^3$, and the electrical resistance was 4.20 x 10$^{-6}$ Ω. The product obtained was thermally stable - showed only 9% mass loss at 965 °C.

The glassy carbon was characterized by a varied amount, size and distribution of spherical pores (Fig. 12 b, c). The results of microscopic examinations revealed the occurrence of both porous and non-porous surfaces. Based on Raman analysis (Fig. 13a), it was found that glassy carbon with a generally amorphous structure contained areas of turbostratic structure and areas with a higher structural order. The well-ordered carbon structures in glassy carbon were deduced from the intensity of the bands characteristic of carbon materials, namely, the G-band at 1580 cm$^{-1}$ and D-band at 1350 cm$^{-1}$. The positions of these two bands in the spectrum of glassy carbon were similar to their locations in the spectrum of natural graphite. However, the high ratio of the intensities of the D- and G-bands ($I_D/I_G$=1.4) for glassy carbon revealed the predominance of the disordered carbon structure and confirmed its mixed structure.
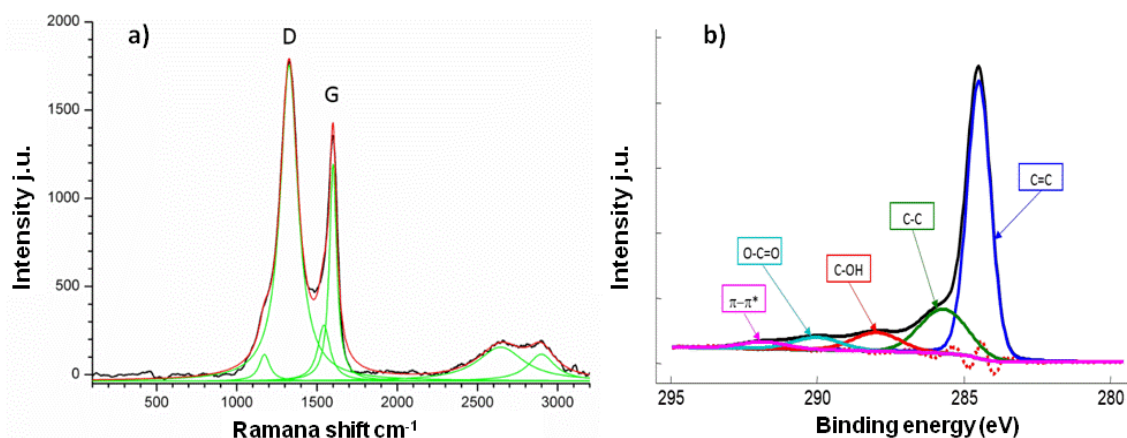


**Fig. 13**. a) Raman spectrum and b) C1s core line via XPS spectroscopy of glassy carbon.

Information on the structure of glassy carbon was verified and confirmed by detailed analysis of the C1s core line using the XPS method. In addition to the primary and most intense peak with a binding energy of 284.5 eV and a peak at 291.9 eV associated with the presence of the graphite structure, a band was also observed with an energy of 285.7 eV, which is characteristic for sp$^3$ carbon bonds in a disordered carbon structure.

The other bands observed on the C1s core line were associated with the presence of oxygen groups, i.e., hydroxyl, carbonyl and ether [35]. The heterogeneity of the glassy carbon surface and the presence of functional groups in its structure led to strong interactions and bonds, including covalent bonds, with polymer moieties in composites with the participation of glassy carbon.

The carbon materials of various shapes, geometries and properties described and characterized in the **H1-H3** and **H7-H10** works have been used as fillers for polymer composites.

## IV. POLYMER-CARBON COMPOSITES

The aim of the research on polymer-carbon composites was to determine the relationship between the structure (primarily the degree of structural order) and properties of different carbon fillers and the morphology and properties of the final materials. Individually in binary composites and in various combinations in hybrid composites, the natural and synthetic carbon materials described in Chapter 3 were used as micro- and nanofillers for polymer-carbon composites. Epoxy resins and cyanate resins were considered as the polymer matrix.

### IV.1. COMPOSITES WITH NATURAL CARBON FILLERS [H1-H3, H7, H10, H12]

Despite the intensive studies on the use of graphene materials as polymer fillers, natural carbon materials with various degrees of organic matter metamorphism, such as bituminous coals and anthracites, are still treated marginally as potential counterparts, despite their positive properties and low costs of production. These materials are composed of polyaromatic carbon layers in the form of stacks with different order degrees and could be used as a promising precursor of multi- and several-layered graphene structures. The literature contains few reports on the use of natural coals with various metamorphism, including bituminous coals and anthracite, in polymer-carbon composites. These works primarily address introduction of the appropriate fraction of bituminous coals into the thermoplastic matrix [36, 37].

The main objective of research described in **H1**-**H3** was to answer the question of how poorly ordered coal containing various functional moieties influences the properties of its epoxy composites. Powdered bituminous coal from the Bielszowice mine with a size of less than 80 μm was dispersed in an epoxy resin and subsequently cross-linked with novolac resin.

In **H1**, the effect of coal particles on the morphology and thermomechanical properties of epoxy composites (also including CTBN or ETBN rubber (6 mass%) in addition to carbon filler) was investigated. Microscopic observations (OM, TEM) confirmed that the carbon filler particles significantly affected the process of rubber separation and the final morphology of epoxy-carbon composites (Figure 14).
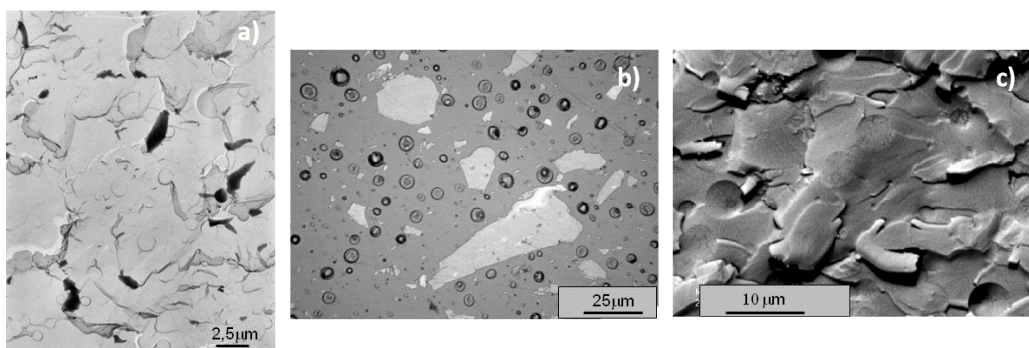


**Fig. 14.** Microphotographs of epoxy composite (EP/NZ) with ETBN and carbon filler: (a) TEM (**H1**), (b) optical microscopy (**H1**), (c) SEM (**H3**).

Carbon filler in the form of particles with a broad size distribution and irregular shape that were uniformly dispersed in the epoxy matrix did not form agglomerates. The fracture surface of a composite containing coal particles (Fig. 14c) was more disturbed compared with the brittle fracture of the neat epoxy matrix (Fig. 1a). Surface deformations were associated with the presence of filler. Good adhesion of the filler particles to the epoxy resin was the main reason for the lack of voids and gaps at the filler-polymer interface. In the case of composites modified with ETBN (Fig. 14b, c), the presence of carbon material influenced the phase separation of the rubber, resulting in heterogeneous spherical rubber domains of much larger dimensions, up to 30 μm, compared with the particle diameters of 0.3-3 μm in the modified epoxy matrix without carbon filler (Fig. 1b).

DMA studies have shown that powdered coal used as carbon filler improved the viscoelastic properties of epoxy composites, including the storage modulus, loss modulus and mechanical loss factor in the glassy and rubbery-like states. A particularly noticeable effect of filler particles on the storage modulus was observed in the plateau region after the glass transition. In this area, a greater than two-fold increase occurred in the composite modulus value with coal and ETBN in contrast to the pure EP/NZ matrix modified with ETBN. The carbon filler slightly increased $T_g$ and decreased the intensity of tan $\delta$ due to the reduced mobility of the epoxy network fragments in the glass transition region.

It was found that powdered coal filler increased the stiffness of its epoxy composites, but unfortunately, it also decreased the flexural mechanical strength. The strength deterioration of epoxy-carbon composites can be assigned to the poorly ordered internal structure of bituminous coal with a medium metamorphism degree (Chapter 3).

The introduction of reactive CTBN or ETBN rubbers did not lead to improvement of the mechanical properties of three-phase composites. The presence of carbon material disturbed the phase separation of the rubber, resulting in heterogeneous spherical rubber domains of much larger dimensions, up to 30 μm, compared with the particle diameters of 0.3-3 μm in the modified epoxy matrix without carbon filler. These domains were significantly larger than in the carbon-free system (Figure 11b), and their dispersion in the final composite was not homogeneous, which contributed to the mechanical weakening of composites.

**H3** determined the influence of bituminous coal particles on the mobility of the main chains and smaller fragments of the epoxy network. For this purpose, the viscoelastic properties of the epoxy composites in its β- and α-transition regions were investigated, both as a function of temperature and oscillation frequencies. The studies were performed for an epoxy composite with carbon filler particles (16 mass%) and composites also containing ETBN or CTBN rubber domains.

It was observed that despite the restriction of epoxy network mobility, the addition of carbon filler did not change the character of β- and α-transition in epoxy-carbon composites. In contrast, the ETBN rubber particles in the epoxy-carbon composites increased the temperature range of the glass transition compared with the pure epoxy matrix and the epoxy composite with only coal particles. Similar results were obtained for

the epoxy-carbon composite modified with CTBN. This behavior demonstrated that the rubber domains influenced the nature of the glass transition of the epoxy network because of the higher heterogeneity of the polymer phase and the chemical interactions between the carboxyl and epoxy moieties of rubbers with the functional groups of the epoxy matrix.

Additionally, the influence of bituminous coal particles on the kinetics of the cross-linking reactions between epoxy resin and novolac resin was studied. The epoxy matrix modified with CTBN or ETBN was also examined, and the results were described in **H2**. The conversion changes during the cross-linking process were determined using the total and residual heats of reaction from DSC measurements. The activation energy was determined under isothermal and non-isothermal conditions.

The time dependences of the isothermal conversion rate and the cross-linking reaction rate confirmed that the carbon filler did not change the reaction mechanism but affected the cross-linking rate at the initial stage and at the later step. This observation was evidenced by the increase in the reaction rate coefficients and the lower activation energy. The acceleration of cross-linking by the carbon filler can be explained by the effect of functional groups (mainly oxygen in the form of hydroxyl, carboxyl, ether, and epoxy) on the surface of filler particles. The effect of carbon particles on the cross-linking rate was lower when ETBN rubber was present in the reaction mixture. For this three-phase composite, a lower reaction coefficient and higher activation energy were observed at the later cross-linking step. In addition to the effect of the functional groups of the coal on the cross-linking reactions, the interactions of the filler functional groups with the polymer matrix had a positive influence on the quality of the filler particle dispersion by limiting their sedimentation and agglomeration.

The results for epoxy-carbon composites reported in **H1**, **H2** and **H3** revealed that microparticles of natural bituminous coal clearly improved the thermal resistance and stiffness (dynamic modulus of elasticity and Young's modulus) of composites. However, composites containing this filler were characterized by a lower mechanical strength, which was the main reason for further investigations on carbon materials used as fillers that could contribute to improved mechanical properties of the final polymer composites.

In **H7**, the initial Svierdlovski anthracite (SVraw) characterized by a poorly ordered turbostratic structure, and SV2000 anthracite with a graphite-like structure containing well-ordered graphene layers were used as carbon fillers in epoxy resin (Chapter 3). The purpose of this study was to determine the effect of the degree of graphene sheet order on the cross-linking of the epoxy resin with aliphatic amine and the morphology and properties of the new epoxy-carbon composites. The effect of SV2000 anthracite as a filler was compared with that of well-defined graphite. Observations were conducted for epoxy composites containing 5 to 30 mass% of anthracite fillers.

Microscopic investigations showed that the structure of the anthracite fillers influenced the fracture surface morphology of the epoxy-carbon composites (Fig. 15).
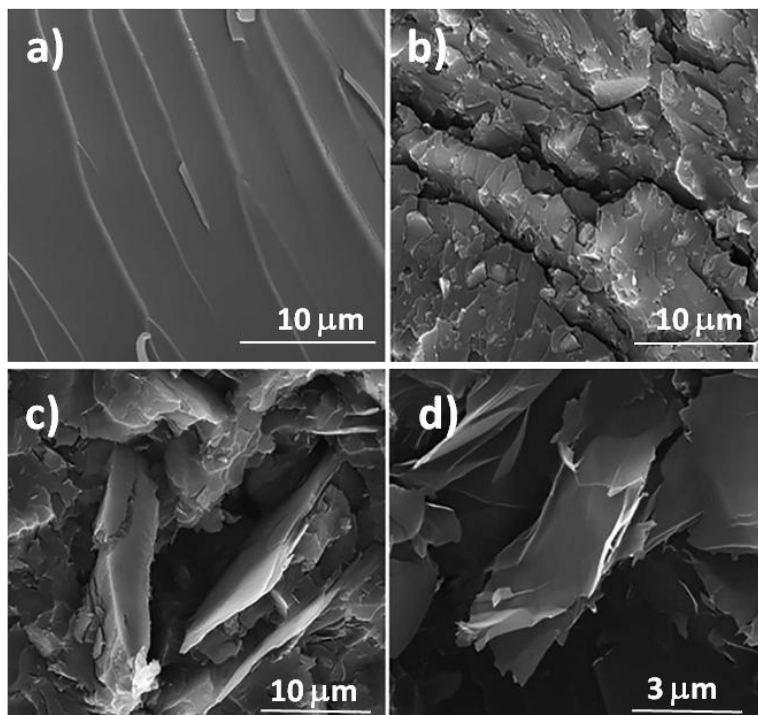
**Fig. 15.** SEM fracture surface microphotographs: (a) epoxy matrix, (b) composite with SVraw (10 mass%), (c) composite with SV2000 (10 mass%), (d) composite with graphite (10 mass%).

The fracture surface of composites with anthracite was distorted and deformed compared with the smooth brittle surface that is characteristic of epoxy resins. The filler particles exhibited good adhesion to the epoxy matrix, participated in energy absorption during failure and remained in the continuous polymer phase. The formation of the plastic flow areas in the polymer matrix and its substantial deformation associated with the presence of filler particles led directly to an increase in mechanical strength. The fracture morphology of the composite with structurally well-ordered SV2000 anthracite was similar to the fracture surface of the composite with graphite (Fig. 15d).

Preparation of composites requires detailed knowledge of the filler effect on the cross-linking reaction rate and the activation energy. The thermal effects studied by DSC method showed that SVraw anthracite accelerated cross-linking of the epoxy resin at its initial stage. As determined using the Flynn-Wall-Ozawa and Kissinger models [18, 19], the activation energy was decreased in the presence of SVraw and appears to be associated with an accelerating effect of the functional species, (mainly hydroxyl and carboxyl) attached to the carbon surfaces, according to the autocatalytic mechanism [H2]. However, the influence of other factors, e.g., thermal conductivity, should also be considered. Elimination of most of the oxygen species in anthracite SV2000 after its thermal treatment suggested that this filler did not affect the activation energy of the epoxy resin cross-linking.

The influence of the structural order degree and content of carbon fillers on the storage modulus, loss modulus and tan $\delta$ coefficient measured by DMA were determined for the epoxy composites. In the case of all composites with anthracite fillers, the storage modulus was greater throughout the temperature range compared with the modulus of the epoxy

matrix. The anthracite fillers facilitated a slight increase in the $T_g$ of composites, on average 2-3 °C, which could be assigned to a certain restriction of the mobility of the epoxy network by the filler particles.

In addition to their advantageous viscoelastic properties, the epoxy composites filled with structurally different anthracite fillers (SVraw and SV2000) were characterized by a significant improvement in mechanical strength (up to 60%). The pure epoxy matrix and epoxy-anthracite composites were thermally stable without registered mass loss at up to 350 °C. Thermal degradation of the epoxy network above 350 °C occurred in a narrow temperature range. It was found that the structure of the anthracite filler had no effect on the temperature range of the polymer network degradation. However, the increase in the filler content contributed to a lower mass loss of the composites at temperatures above 500 °C.

The advantage of the application of anthracite materials with different structural orders as composite fillers is the possibility of their use without chemical or physical functionalization. This work proved that to achieve the desired mechanical and electrical properties, it is necessary to use a significant amount of filler in preparation of valuable composites.

A principal objective of **H10** was the use of new nanofillers of epoxy composites, i.e., graphenic materials obtained by chemical functionalization of SV2000 anthracite with graphite-like structure by two different methods (Chapter 3). It was shown that the use of only 0.5 mass% of these functionalized fillers allowed to obtain composites with properties comparable to those of epoxy composites with SVraw or SV2000 anthracite with filler content of 20-30 mass%.

Studies on the thermomechanical properties of nanocomposites with both reduced anthracite SV2000 oxide and anthracite functionalized by cycloaddition of azomethine ylide confirmed a 40-45% increase in storage modulus and a 40-51% improvement in strength compared with the pure epoxy matrix. Epoxy nanocomposites with functionalized anthracite fillers were compared with analogous composites produced using commercially available graphene nanoplatelets of similar size and numbers of graphene layers (XY surface $\leq 14 \mu$, thickness 10-20 nm). The results showed that composites with both reduced anthracite oxide and anthracite functionalized by ylide cycloaddition had better viscoelastic properties and better mechanical strength than composites with graphene nanofiller.

In addition to the relevant mechanical properties, an important requirement for polymer composites is the preparation of electrically and thermally conductive materials. Unfortunately, composites with anthracite fillers showed a notably high percolation threshold of electrical properties. To achieve a composite with an electrical conductivity on the order of $10^{-8}$ -$10^{-6}$ Sm, it was necessary to use up to 30 mass% anthracite SV2000, which was a major drawback in the preparation of composites.

For composites based on polyethylene and polypropylene the solution to this problem could be the so-called segregated composites. Prior to basic processing of such composites,

conductive filler particles were located at the boundary between the polymer grains, and after polymer hot compression, an ordered network of conductive filler paths was created.

**H12** describes research on the electrical properties and electromagnetic radiation shielding efficiency of segregated composites with an ordered distribution of carbon filler particles. High-molecular weight polyethylene (UHMWPE) and polypropylene (PP) were used as the polymer matrix, and anthracite SV2000 was used as a carbon filler. To investigate the effect of the composite preparation method on the electrical properties, two types of composites were obtained: composites with an ordered distribution of the SV2000 particles (i.e., segregated) and conventional composites with random SV2000 particles distributed in the matrix. Segregated composites were obtained by initial mixing of plastic grains with SV2000 anthracite. As a result of electrostatic interactions, the filler covered the surface of the plastic particles. The mixture was subsequently compressed at elevated temperature under pressure. Conventional composites were prepared by the extrusion method.

The morphology of segregated composites with SV2000 as filler varied depending on its amount (Fig. 16). The filler was embedded between the polymer particles, and the thickness of the filler layers increased with their contents. When the content of anthracite reached the percolation threshold ($\phi \cong 3$ vol.%), filler layers formed in the polyethylene matrix conduction paths of sufficient thickness providing a noticeable improvement in electrical conductivity (Fig. 16b).
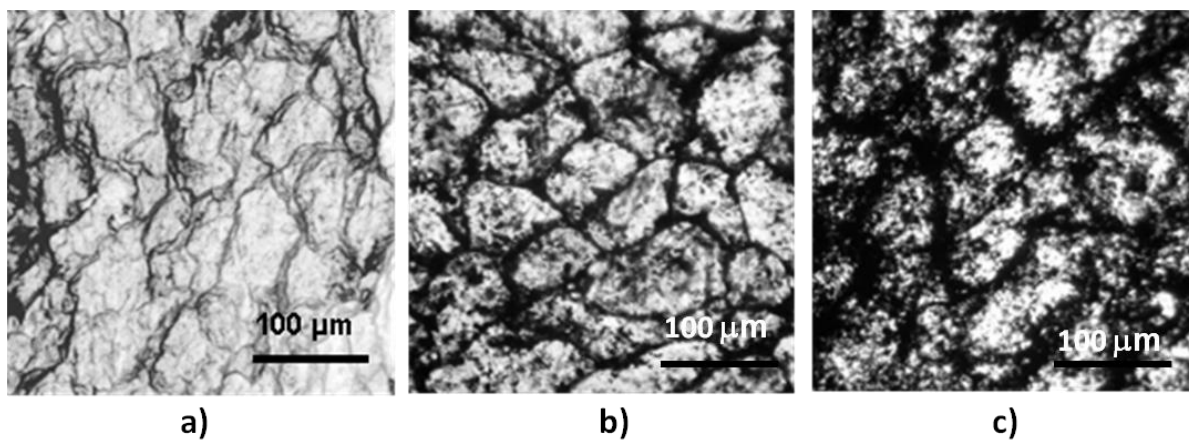


a)                                        b)                                        c)

**Fig. 16**. Formation of conductive filler phase in a segregated UHMWPE composite containing a) 1 vol.% SV2000, b) 3 vol.% SV2000, c) 5 vol. % SV2000.

The effect of filler content on the electrical conductivity and electromagnetic shielding efficiency of segregated and conventional composites with SV2000 was determined. These studies showed that the percolative nature of conductivity changes and determines the percolation threshold values. In segregated composites, the threshold content of SV2000 drops to 2.95 vol.% compared with the high percolation threshold observed in conventional composites with SV2000 (24.8 vol.%). This content significantly approaches percolation thresholds of 0.21 and 0.55 vol.%, for nanocomposites with graphene nanoplatelets and thermally expanded graphite were used in the role of carbon fillers, respectively.

The increase in the electrical conductivity of composites with increasing carbon filler content led to significantly improved electromagnetic shielding efficiency due to the multiple and repeated reflections of these waves from the carbon scaffolding in segregated systems.

The studies of polymer composites with naturally occurring carbon fillers display an enormous diversity of their properties and indicate the possible use of various readily available natural carbon materials to modify the properties of the composites.

## IV.2. COMPOSITES WITH SYNTHETIC CARBON FILLERS [H6, H8, H9, H11]

In recent years, many studies have been performed on carbon materials such as carbon nanotubes or graphene nanoplatelets synthesized from various precursors using physical (laser, plasma, thermal) and chemical methods (oxidation, CVD) [4-10]. Because of their specific properties, these materials are often used as fillers in polymeric composites and also in combination with other fillers.

Furthermore, an entire range of products obtained during pyrolysis of coal, petroleum, biomass, vegetable and polymeric precursors can be considered as synthetic carbon materials. In contrast to the highly ordered structure of carbon materials consisting of graphene units, these materials are characterized by local-only structural ordering in mostly amorphous carbon structures with high porosity and low apparent density.

Subsequent publications included in the *scientific achievement* refer to the use of synthetic carbon materials such as glassy carbon, also in combination with carbon nanotubes **[H9]** and particulate carbon foams **[H11]**, as composite fillers. These research studies focused primarily on composites containing one type of carbon filler but also included multi-phase hybrid composites that, when used simultaneously, combine the advantages of at least two carbon fillers of different structure, shape and properties **[H9]**.

In connection with the commencement of my own research on the preparation and characterization of hybrid composites containing at least two carbon fillers, review paper **H6** on this subject was prepared. The main purpose of this work was to develop an in-depth analysis of the current state of knowledge of hybrid carbon composites, with a particular emphasis on the synergistic effect of the use of fillers with different geometries and properties. The behavior of various nanofillers applied simultaneously results from the formation of a more efficient network of connections between their particles than in the case of one type of filler and is responsible for the additional improvement of important composite properties [38, 39].

For representative examples of various hybrid polymer composites with the use of inorganic and metallic nanofillers, observations included a greater positive synergistic effect than that arising only from the participation of individual fillers and improved composite properties such as thermal conductivity and electrical and mechanical characteristics. Additionally, the listed studies demonstrate that combination of the advantageous properties of different fillers can lead to a negative synergistic effect (contrary to expectations) in certain cases.

**H9** describes research on the use of a proper glassy carbon fraction (with high mechanical strength and good thermal and electrical conductivities) as a filler in binary and hybrid epoxy composites. Such polymer-carbon composites have not yet been studied, to the best of my knowledge. The only existing references are related to the use of a glassy carbon fraction of more than 40-100 μm as a filler in metal alloys [40] and cross-linked phenol-formaldehyde resin [41].

The isometric grains of glassy carbon, with a bimodal size distribution in the range of 0.05-0.2 μm and 6.6-10 μm, were used in amounts of 5 to 20 mass% for preparation of binary epoxy-carbon composites. Closed pores of different sizes appearing in the glassy carbon were not connected to each other and were homogeneously distributed. For preparation of hybrid composites, multi-walled carbon nanotubes with a diameter of 5-9 nm and up to 5 μm in amounts of 0.5 mass% were used in addition to the glassy carbon.

Subsequently, the effect of glassy carbon grains used alone and in combination with carbon nanotubes on the morphology, interfacial interactions and adhesion between these fillers and the polymer were investigated in binary and hybrid composites. The mechanical, thermal and electrical properties of binary and hybrid epoxy composites were also discussed.

SEM microscopy studies showed that in both types of composites, glass carbon particles formed a homogeneous dispersion in the epoxy matrix. The lack of a clear boundary between the filler and the epoxy matrix (Fig. 17b) demonstrated the excellent adhesion of the carbon particles to the polymer phase.
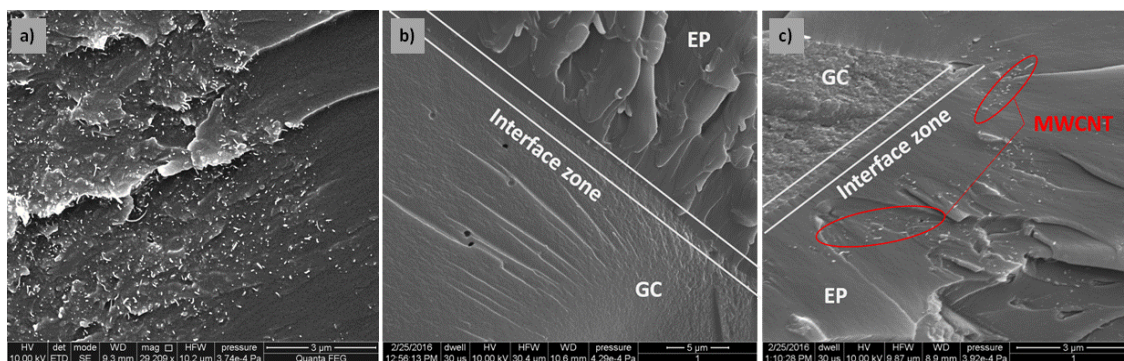


**Fig. 17.** Interface area for composite: a) binary with carbon nanotubes, b) binary with glass carbon, b) hybrid with carbon glass and carbon nanotubes.

Despite the use of various methods to obtain good quality dispersion in the epoxy resin, carbon nanotubes used individually in nanocomposites without glassy carbon formed areas of homogeneous dispersion and areas with evidently agglomerated nanotubes (Fig. 17a).

The presence of the glassy carbon microparticles in the hybrid composites clearly reduces the agglomeration tendency of the carbon nanotubes. The nanotubes were dispersed more evenly in the areas between the glassy carbon grains (Fig. 17c). The agglomeration-limiting tendency of carbon nanotubes by introduction of a second filler in the hybrid composites is known for various combinations of fillers, not only carbon (nanotubes/carbon black, nanotubes/graphene nanoplatelets, nanotubes/montmorillonitre) **[H6].**

The use of DMA method allowed detailed assessment of the glassy carbon effect, also in combination with carbon nanotubes, on the dynamic modulus of elasticity and glass transition temperature of the studied composites, the dispersion of the filler in the matrix and the interfacial interactions between them.

Carbon nanotubes improved the storage modulus of hybrid composites, both in glassy and rubbery-like states, compared with binary composites with only glass carbon. The reason for the increase in stiffness expressed by the modulus growth was the homogeneous dispersion of nanotubes between the glassy carbon particles in the epoxy matrix and the strong interactions between the fillers and the polymer. Uniform dispersion of nanotubes also affected reduction of the tan $\delta$ peak intensity and the greater vibration damping ability of the hybrid composite. The introduction of both glass carbon and carbon nanotubes restricted the mobility of the epoxy network chains in binary and hybrid composites, as evidenced by the increase in $T_g$ by several degrees.

The synergistic effect resulting from simultaneous use of glassy carbon and carbon nanotubes was also observed for the mechanical strength and electrical conductivity of the hybrid composites. The largest increase in the mechanical strength (33%) was observed for the composite containing nanotubes and 10 mass% of glassy carbon compared with the epoxy matrix. The increase in the glassy carbon content of the hybrid composite to 20% resulted in a 53% greater Young's modulus compared with the polymer matrix and 29% greater compared with the hybrid composite containing 10 mass% glassy carbon. However, the mechanical strength of this composite was 17% lower than for the hybrid composite with 10 mass% glassy carbon.

Reinforcement of the viscoelastic and mechanical properties of hybrid composites compared with those of the binary system epoxy matrix/glassy carbon was attributed to further diminishing effects of the internal stresses in the epoxy matrix by carbon nanotubes dispersed between GC particles.

Carbon fillers, both glassy carbon and carbon nanotubes, are characterized by good electrical conductivity, and their presence improves the electrical properties of the composites compared with the polymer matrix. The greatest improvement in electrical conductivity was observed for a hybrid composite containing 10 mass% of glassy carbon. The specific resistance determined for this composite was lower by 11 orders of magnitude than that of the non-conductive epoxy matrix and a factor of 4 times compared with that of binary composites with glassy carbon. The use of nanotubes in hybrid composites was crucial to enabling more effective transport of electric charges by formation of additional connections and conductive paths between the nanotubes and glassy carbon particles.

No further increase in conductivity was observed by increasing the number of glassy carbon particles to 20 mass%. The main factor limiting the proportional decrease in resistance with increasing filler content was the occurrence of the well-known barrier effect that inhibits the flow of electrons at the interface between the filler and polymer (review **H6**). The

disadvantageous influence of this phenomena on the resistivity of the composite increased with increasing interfacial surface when higher filler contents were used.

Binary and hybrid epoxy composites with glassy carbon are new carbon/polymer materials that meet all the conditions required to effectively and economically replace conventional molding compounds used in protection moldings and wear-resistant, lightweight and highly formable parts with heat dissipation ability and exchange of electric charge.

The use of carbon foam (another type of porous carbon material) as a particulate filler for polymer composites was proposed in **H11**. A thorough study of the effect of carbon foam obtained by carbonization of epoxy resin cross-linked with novolac resin on the properties of their epoxy composites has been reported.

Carbon foam was used as a fraction of particulate particles with dimensions that preserve the unique structure of the foam and its valuable properties. The irregular grains of carbon material, which are characterized by a wide particle size distribution of 5 to 250 µm, were introduced in amounts of 5, 10 and 20 mass% to epoxy resins (diglycidyl ether of bisphenol A) cross-linked by an aliphatic amine. The positive effect of this filler on the properties of the polymer composites was expected due to the advantageous properties of the foams such as high hardness, wear resistance, high thermal stability and non-flammability.

The effect of carbon foam particles on the morphology, viscoelastic properties, thermal properties, flammability, coefficient of friction and wear resistance of related epoxy composites has been studied and interpreted. Polymer-carbon composites with particulate carbon foams and glassy carbon have not yet been studied according to my knowledge. The literature references related to composites with carbon foams are limited to the use of various polymer, ceramic and inorganic materials introduced to the precursor at the stage of carbon foam preparation to improve the properties of carbon foams (mainly the mechanical properties) and include impregnation of final porous material [42-44].

Microscopic observations followed by structural image analysis enabled evaluation of the particle shapes, the distances between them and interfacial boundary in a continuous polymer phase. They confirmed homogeneous dispersion and excellent adhesion at the interfacial interfaces (Fig. 18).
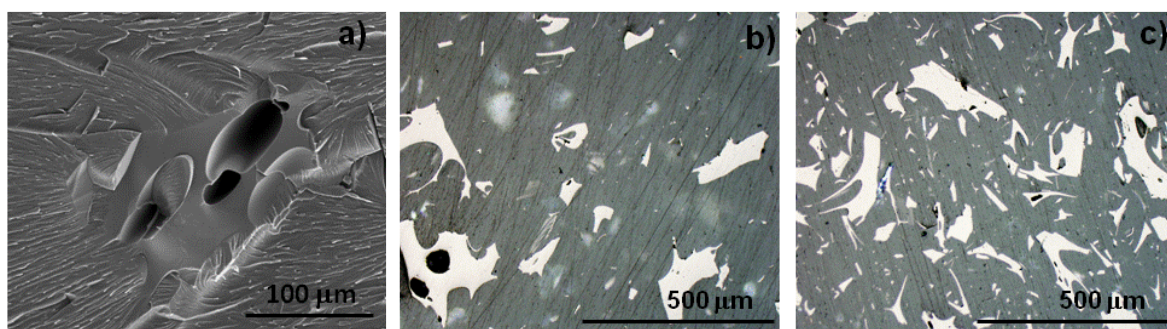


**Fig. 18.** Microphotographs: a) SEM of composite with 10 mass% of carbon foam, b) OM of composite with 5 mass% of carbon foam, c) OM of composite with 20 mass% of carbon foam.

With the introduction of carbon foam particles, it has become possible to achieve a two-fold increase in the storage modulus of composites compared with the modulus of the polymer matrix. Foam particles dispersed in a polymer matrix influenced the dynamics of motion of the molecular chains by restricting mobility of the epoxy network, resulting in an increase in the glass transition temperature of 2 to 8 °C.

The effect of the volume fraction of the carbon foam particles on the efficiency factor of this filler (r) was determined based on the growth of the storage modulus of the composites relative to the modulus of the polymer matrix. In the glassy state, the highest coefficient was observed for the composite containing 5 mass% filler. An increase in the filler content (10, 20 mass%) resulted in a decrease in the efficiency factor, most likely due to abnormal stress at the interface between the polymer and filler grains, despite their excellent adhesion.

In contrast to the glassy state of the notably limited mobility of the network fragments, in the rubber-like state, the highest value of the efficiency factor was observed for the composite with 20 mass% of filler. Above the $T_g$, a greater number of carbon particles act as a specific skeleton that reinforces the polymer structure. Hardness measurements of composites reinforced with dispersed foam particles showed that the composite with 20% filler was characterized by a hardness that was almost 4-fold higher than the hardness of the epoxy matrix.

It has been found that the carbon foam particles in the composites improves the friction coefficient and wear resistance. For all epoxy composites with carbon foam, the coefficient of friction is reduced by a factor of approximately two, and the wear of the composite material is unnoticeable compared with the wear of the epoxy matrix without the filler.

The flammability of epoxy composites with carbon foam as determined using a conical calorimeter has shown that the addition of thermally stable carbon foam significantly changed the fire-retardant behavior of the final composites. A clearly visible increase in the ignition and flameout times was observed for all epoxy composites, whereas a serious improvement in burning resistance was reflected for 10 and 20% of carbon foam micropieces. The delayed ignition time was accompanied by lower values of total heat release and mass loss rate for the polymer/carbon composite materials.

Polymer composites with the appropriate particulate carbon foam fraction as a filler appear to be promising as light and easily recyclable materials characterized by high wear resistance. The study of flame resistance of the composites is an important advantage for use of these materials in high temperature conditions.

A production method for binary and hybrid polymer-carbon composites consisting of particulate carbon foams used as a filler in a continuous matrix of various polymer materials was the subject of patent descriptions [App. V, item II/B-3].

## V. SUMMARY

Composites with various carbon fillers dispersed in polymer matrices are materials that exhibit many valuable physical and chemical properties, facilitating applications in conditions of elevated temperature, pressure and exposure to environmental factors.

The summary of my results described within the framework of *scientific achievement* describes the influence of the structure and properties of polymer networks and carbon fillers (including interfacial interactions and compatibility of individual components) on the morphology and final properties of new polymer-carbon composites. Using the appropriate selection of polymer matrix and carbon fillers, these studies were designed to obtain new composite materials with advantageous mechanical and thermal properties and the ability to conduct electrical charge.

Observations of the cross-linking reactions for epoxy resins and cyanate esters in the presence of elastomeric modifiers have shown improvement in the mechanical properties after cross-linking, especially for impact strength, while maintaining a sufficiently good thermal resistance. These results mean that the polymer matrices modified in this manner are more suitable for applications in polymer-carbon composites.

For use as fillers in both binary and hybrid composites, natural carbon materials of different structural order and synthetic porous carbon materials that were not previously used, were proposed.

Thermal modification of anthracite (up to 2000 °C) led to obtain a group of fillers with different structural order, from a poorly ordered turbostratic structure in the case of the initial anthracite to a graphite-like structure with a high degree of graphene sheet order. The use of these anthracite materials as fillers in epoxy resin revealed that the increasing order of their layered structure improved the viscoelastic, mechanical and thermal properties of the final composites produced.

Anthracite fillers, despite their positive effect on thermo-mechanical properties, exhibited a high percolation threshold of electrical conductivity for polymer composites containing them. In the case of thermoplastics, a proper procedure for preparation of segregated composites by the hot compression method resulted in an ordered distribution of filler particles in the polymer matrix. The formation of conductivity paths allowed for a tenfold decrease in the filler percolation threshold for polymer-anthracite segregated composites compared with that of conventional dispersed composites.

Chemical functionalization of well-ordered anthracite using an oxidative improved Hummer method followed by thermal reduction and dienophile cycloaddition of azomethine ylide led to new graphenic nanofillers with properties similar to those of commercially available graphene nanoplatelets with comparable dimensions and aspect ratio.

The use of chemically functionalized anthracite with a graphenic structure composed of separated graphene layers as a filler allowed a significant reduction in the amount of carbon material used in the epoxy composites. The thermo-mechanical properties of

nanocomposites with only 0.5 mass% anthracite nanofillers were comparable to the properties obtained for composites with 20-30 mass% of conventional anthracite fillers.

The procedure proposed for production of carbon foams from polymeric precursors: cyanate esters modified with epoxy resin and epoxy resin cross-linked with novolac resin allowed to  prepare porous fillers with a highly advantageous structure, high hardness and wear resistance, thermal stability and electrical and thermal conductivities.

Porous carbon materials with micrometer dimensions have been used to produce binary polymer-carbon composites and hybrid composites with the application of additional carbon nanotubes. The concept of using particulate glass carbon and carbon foams as a filler to retain their specific porous structure resulted in composites with notably good mechanical and thermal properties, wear resistance and low friction coefficient.

The research results presented in *scientific achievement* have proved that use of the proposed carbon materials as fillers in polymers opens up wide possibilities in the design of new polymer-carbon composites with the desired properties.

## References:

1. Florjańczyk Z., Penczek S. (Eds). Chemia polimerów, II i III. Oficyna Wyd. Pol. Warszawska, 1995-98.
2. Galina H. Fizykochemia polimerów. Oficyna Wydawnicza Politechniki Rzeszowskiej, 1998.
3. Królikowski W., Rosłaniec Z. Nanokompozyty polimerowe. 2004. KOMPOZYTY (COMPOSITES) 4, 9.
4. Haupert F., Wetzel B. Reinforcement of thermosetting polymers by the incorporation of micro- and nanoparticles. In: Friedrich K, Fakirov S, Zhang Z (eds). Polymer composites from nano- to macro-scale. Springer Science+Business Media, Inc. 2005, pp. 45–62.
5. Sengupta R., Bhattacharya M., Bandyopadhyay S., Bhowmick A. K. A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. 2011. Prog. Polym. Sci. 36, 638–70.
6. Sadasivuni K. K., Ponnamma D., Thomas S., Grohens Y. Evolution from graphiteto graphene elastomer composites. 2014. Prog. Polym. Sci. 39 (4), 749-780.
7. Sichel E. K. Carbon black-polymer composites: the physics of electrically conducting composites. M. Dekker, 1982.
8. Donnet J., Bansal R. C., Wang M. J. Carbon black: science and technology. 2nd ed. CRC Press, 1993.
9. Fu S.-Y., Mai Y.-W., Lauke B., Yue C.-Y. Synergistic effect on the fracture toughness of hybrid short glass fiber and short carbon fiber reinforced polypropylene composites. 2002. Mater. Sci. Eng. A 323, 326–35.
10. Spitalsky Z., Tasis D., Papagelis K., Galiotis C. Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. 2010. Prog. Polym. Sci. 35, 357–401.
11. Horie K., Hiura H., Souvada M., Mita I., Kambe H. Calorimetric investigation of polymerization reactions. III. Curing reaction of epoxides with amines. 1970. J. Polym. Sci.-Polym. Chem. 8, 1357-1372.
12. Kamal M. R. Thermoset characterization for moldability analysis. 1974. Polym. Eng. Sci. 14, 231-239.
13. Kamal M. R., Sourour S. Kinetics and thermal characterization of thermoset cure. 1973. Polym. Eng. Sci. 13, 59-64.
14. Shechter L., Wynstra J., Kurkjy R. P. Glycidyl Ether Reactions with Amines. 1956. Ind. Eng. Chem. 48 (1), 94–97.

15. Kim W. G., Lee J. Y. Contributions of the network structure to the cure kinetics of epoxy resin systems according to the change of hardeners. 2002. Polymer 43, 5713-5722.

16. Lu M., Shim M., Kim S. Effect of filler on cure behavior of an epoxy system: Cure modeling. 1999. Polym. Eng. Sci. 39 (2), 274–285.

17. Wise C., Cook W., Goodwin A. CTBN rubber phase precipitation in model epoxy resins. 2000. Polymer 41 (12), 4625–4633.

18. McKee C., Mortimer M. The effect of temperature on the rate of a chemical reaction. In: Mortimer M., Taylor P. (eds), Chemical Kinetics and Mechanism. Royal Society of Chemistry, 2002.

19. Kissinger H. E. Reaction Kinetics in Differential Thermal Analysis. 1957. Anal. Chem., 29 (11), 1702–1706.

20. Ozawa T. A New Method of Analyzing Thermogravimetric Data. Bull. Chem. Soc. Jpn. *1956*, 38 (11), 1881–1886.

21. Ferry J. D. Viscoelastic Properties of Polymers. 3 rd ed., Wiley, NY, 1980.

22. Martin M. D., Ormaetxea M., Harismendy I., Remiro P. M., Mondragon I. Cure chemo-rheology of mixtures based on epoxy resins and ester cyanates. 1999. Eur. Polym. J. 35, 57–68.

23. Ormaetxea M., Hamerton I. Chemistry and technology of cyanate ester resins. Glasgow: Blackie Academic, 1994.

24. Dinakaran K., Alagar M. Preparation and characterization of cyanate ester-epoxy interpenetrating matrices/organoclay nanocomposites. 2003. Polym. Adv. Technol. 14 (8), 574-585.

25. Van Krevelen D. W. Coal. Topology-Physics-Chemistry-Constitution, Elsevier, 1993

26. Duber S., Rouzaud J. N. Calculation of reflectance values for two models of texture of carbon materials. 1999. Int. J. Coal Geol. 38 (3–4), 333–348.

27. Kwiecinska B. K., Petersen H. I. Graphite, semi-graphite, natural coke, and natural char classification—ICCP system. 2004. Int. J. Coal Geol. 57, 99-116.

28. Ferrari A. C. Raman spectroscopy of graphene and graphite: disorder, electronephonon coupling, doping and nonadiabatic effects. 2007. Solid State Commun. 143, 47-57.

29. Potgieter-Vermaak S., Maledi N., Wagner N., Van Heerden J. H. P, et al. Raman spectroscopy for the analysis of coal: a review. 2011. J. Raman Spectrosc. 42, 123-129.

30. Marcano D. C., Kosynkin D. V., Berlin J. M., Sinitskii A., Sun Z., Slesarev A., et al. Improved synthesis of graphene oxide 2010. ACS Nano 4, 4806-4814.

31. Bourlinos A. B., Georgakilas V., Zboril R., Steriotis T., Stubos A. K. Liquid-phase exfoliation of graphite towards solubilized graphenes. 2005. Small 5, 1841-1845.

32. Hiroshi S. Some Physical Properties of Glassy Carbon. 1962. Nature 193 (4812), 261-262.

33. Noda T., Inagaki M. The Structure of Glassy Carbon. 1964. Bull. Chem. Soc. Jpn. 37, 1534–1538.

34. Jenkins G. M., Kawamura K. Structure of glassy carbon. 1971. Nature 231, 175–176.

35. Liao W. H., Tien H. W., Hsiao S. T., Li S. M., Wang Y. S., et al. Effects of multiwalled carbon nanotubes functionalization on the morphology and mechanical and thermal properties of carbon fiber/vinyl ester composites. 2013. ACS Appl. Mater. Interfaces 5, 3975-3982.

36. Yang F., Qu J., Yang Z., Zhou Z. Thermal Decomposition Behavior and Kinetics of Composites from Coal and Polyethylene. 2007. J. China Univ. Min. Technol. 17 (1), 25–29.

37. Stabik J., Chomiak M. Graded epoxy-hard coal composites: analysis of filler particle distribution in the epoxy matrix. 2016. J. Compos. Mater. 50, 1-15.

38. Chatterjee S., Nafezarefi F., Tai N. H., Schlagenhauf L., Nüesch F. A., Chu B. T. T. Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites. 2012. Carbon 50, 5380-5386.

39. Sumfleth J., Adroher X. C., Schulte K. Synergistic effects in network formation and electrical properties of hybrid epoxy nanocomposites containing multi-wall carbon nanotubes and carbon black. 2009. J. Mater. Sci. 44, 3241-3247.

40. Olszówka-Myalska A., Myalski J., Chrapoński J. Influence of casting procedure on microstructure and properties of Mg alloy-glassy carbon particle composite. 2015. Int. J. Mater. Res. 7, 741-749.

41. Myalski J. Kształtowanie właściwości tribologicznych kompozytów zawierających węgiel szklisty. 2011. Wydawnictwo Politechnika Śląska Gliwice, Monography no. 309,.

42. Klett J. In: Scheffler M., Colombo P. (eds). Cellular ceramics: structure, manufacturing, properties and applications. Wiley, Weinheim, 2005.

43. Nagel B., Pusz S., Trzebicka B. Review: tailoring the properties of macroporous carbon foams. 2014. J. Mater. Sci. 49, 1–17.

44. Fawcett W., Shetty D. K. Effects of carbon nanofibres on cell morphology, thermal conductivity and crush strength of carbon foam. 2010. Carbon 48, 68-80.

**5. DISCUSSION OF OTHER SCIENTIFIC ACHIEVEMENTS**

**BEFORE THE DOCTORAL DEGREE**

I started working at the Institute of Carbon Chemistry of the Polish Academy of Sciences in Gliwice in September 1996, just after the defence of my master thesis on the oxidation of 2-isopropylnaphthalene performed at the Department of Organic Chemistry of the Faculty of Chemistry of Silesian University of Technology.

At the beginning, my scientific activity was focused on the research of the effects of different rank coals (from brown coal up to anthracite and shungite) as well as carbon materials, i.e. coke and carbon black, on the cross-linking reactions of epoxy resins and the properties of final polymer-carbon composites. These studies were conducted in the Laboratory of Non-Energetic Use of Coal within the frame of statutory activities, research projects, cooperation with foreign and national scientific institutions as well as with industry.

The principal subject which I dealt with was the research on the use of Polish bituminous coal of medium metamorphism degree for preparation of new polymer-carbon composites with improved thermal resistance. The results were published in national journals: Karbo and Zeszyty Naukowe Politechniki Śląskiej (App. 5, A1-A3) and were used to develop my doctoral dissertation, which was defended in June 2006 at the Faculty of Chemistry of the Rzeszów University of Technology.

Since 1998 I have studied the properties of polymer, carbon and composite materials using thermal analysis techniques that I have become acquainted in the School of Thermal Analysis SAT'2001 organized by the AGH University of Science and Technology and the Polish Society of Calorimetry and Thermal Analysis. In 2003, I presented the results of the research on cross-linking reactions kinetics for epoxy resins and viscoelastic properties of cross-linked epoxy systems as two lectures at the International Conference on Thermal Analysis (CCTA 9) (App. 5, item II/J-5, J-6). The investigations of thermal effects by differential scanning calorimetry (DSC) as well as thermomechanical (DMA) and dielectric (DEA) properties were an important element of characterization of epoxy matrices and epoxy-carbon composites as a part of the doctoral thesis.

Participation in the task titled "Structure-properties relationship of thermoset polymers filled with coal particles" in the framework of a joint French-Polish cooperation and personal exchange program PICS 617 (1998-2000) allowed me to expand the research on the use of Polish bituminous coal of medium degree of metamorphism for preparation epoxy composites with improved thermal resistance (App. 5, item III/A-1). French partner of this program was Laboratoire des Matériaux Macromoléculaires, Institut National des Science Appliquees - CNRS in Lyon. During two stays in Lyon, I performed research on the effect of coal filler particles on rheological properties changing during the reactions of epoxy resin with amine and hydroxyl cross-linking compounds as well as on the mechanical properties of final epoxy-carbon composites. The results obtained were used to prepare the publication (App. 5, P1) and the conference presentations at renowned conferences, including Euro-

fillers'99 and World Polymer Congress IUPAC MACRO 2000 (App. 5, item II/A-1, item III/B-1, B-3, B-8, B-11). Some of these results were also used in my doctoral dissertation.

In 2004 - 2006, I realized the PhD project founded by Ministry of Science and Information Technology No. 0T 00C 012 26 titled "Modified epoxy matrix for hybrid composites with increased thermal resistance" (App. 5, item II/H-5). The aim of this research, in addition to obtain thermally resistant polymer matrix, was to improve the impact strength and resistance to cracks propagation of cross-linked epoxy composites with bituminous coal. The results of these investigations were published in Annals of the Polish Chemical Society (App. 5, A11) and peer-reviewed conference materials (App. 5/A8, B8) and were presented at scientific conferences (App. 5, items II/J-7, J-8).  They also constituted the basis of my doctoral dissertation under the same title as the project.

In addition to investigations mentioned above, I took part in other works on composites with various forms of carbon fibers as the basic reinforcement. Since 1998, the research connected with the hybrid epoxy-carbon moldings including various carbon powders as additional filler to carbon fibers were carried out in cooperation with the Electrotechnical Institute in Wrocław. I participated in the development and preparation of polymer matrix containing powder carbon fillers (brown and bituminous coals) used for saturation process of continuous carbon fibers (roving). Additionally, I investigated the properties of hybrid composites obtained by compression molding and RIM methods (App. 5, item III/B10).

In 2002-2004, I carried out similar research topic related to hybrid epoxy composites with powdered carbon fillers and chopped carbon fibers in the frame of the project „Hybrid epoxy composites with improved impact strength and thermal resistance" (App. 5, item II/H-4).

Additionally to the research on polymer-carbon composites, I participated in the study of epoxy composite materials reinforced with glass fibers and mica materials, realized as a part of cooperation with Izo-Erg S.A from Gliwice. These composites, mainly laminates, were used for electroinsulating and constructional applications as well as materials with a high thermal resistance (App. 5, item II/A-6, item III/B-9, B-12, M-4, M-5).

The topics related to  epoxy composites with glass fibers were also carried out in cooperation with the Institute of Heavy Organic Synthesis ICSO-Blachownia. Additionally, this cooperation concerned the development of new epoxy resins as well as the improvement of flame retardancy of epoxy materials using ammonium polyphosphates and diphenyl phosphate. The results of the joint works were presented at conferences and peer-reviewed conference materials (App. 5, item II/A-4, B-9, item III/B-7).

Cooperation with the Military Institute of Technical Armament in Zielonka was connected with the research of polymer composites with aramid fibers by RTM technology. These works were carried out in the frame of research project titled " Study of dynamic resistance of polymer composites reinforced with aramid fibers and made by RTM technology for elements of weaponry and ammunition equipment" (App. 5, Item II/H-6) coordinated by

Institute of Armament and focused on the appropriate selection of the polymer system to saturation of the fibers used in the components of weapons and ammunition production.

Research Works on the polymer composites mentioned above, focused on matrices based on epoxy and phenol-formaldehyde resins. Whereas, in 2000-2004 I performed the research tasks on application of various coals as fillers of polyolefin plastics in cooperation with the Department of Plastics of Faculty of Mechanical Engineering, Silesian University of Technology. The results of this joint research were presented at conferences and in peer-reviewed conference proceedings (App. 5, item II/A5, A9, item III/B-4, B-13, B-21).

The separate research issue carried out in cooperation with Chemical Plants "Carbochem" in Gliwice was the study of various types of carbon black, also as potential fillers of composites. In 1996-2003 I participated in three key projects involving above mentioned topic. The first of the projects "Start-up of production of carbon black for special purpose materials and composites" (App. 5, item II/H-1) was related to the special carbon black as composite material fillers. Next project, PHARE SCI-TECH II (App. 5, item II/H-2), financed by EU sources "Poland and Hungary: Assistance for Restoring their Economies" was realized in the cooperation between the Institute of Carbon Chemistry, "Carbochem" and the Silesian University of Technology. The last targeted project finished with the launch of the semi-active carbon black (Sakap) production line taking into account the requirements of ASTM, customers and environmental requirements (App. 5, item II/H-3).

Besides, in 1996, 1999, 2001 and 2004, I was a member of Organizing Committee of the cyclic conference, firstly the national conference "New Carbon Materials", which next was transformed into the international conference "New Carbon and Composite Materials" with the subject matter extended with composite materials.

**AFTER THE DOCTORAL DEGREE**

Based on the experience and achievements gained during preparation of my PhD thesis, I have formulated new research topics related to polymer-carbon composites with various types of carbon fillers, both natural and synthesized specially for this purpose. These studies were conducted at CMPW PAN in the Laboratory of Carbon Materials transformed in 2012 to the Laboratory of Carbon and Polymer-Carbon Materials. Most of this work was related to the studies described and discussed in the post-doctoral thesis as scientific achievement as a cycle of H1-H12 publications. These studies were conducted as a part of statutory activities, research projects and international cooperation.

Additionally, I was involved in other research areas in cooperation with other research institutions and with industry. In 2007-2010, I participated in comparative studies of selected physical properties of Polish coals with different coking abilities and their two- and three-component blends. This research focused on the determination of dynamic mechanical properties and the fluidity of binary and ternary blends of coals with notably good coking properties and various additives of poorer-quality carbon materials. The main objective of this work was to investigate the synergistic effect that occurs during thermal

decomposition of binary and ternary mixtures of carbon materials in various proportions using DMA and Gieseler's plastometer. There were found the evident relationships between the measured physical parameters and the contribution of individual coals in the initial blend. These relationships were less pronounced for ternary blends than for two-component mixtures, which indicates more complex character of the interactions between individual coals in mixtures with larger number of ingredients. The observed synergistic effects were confirmed by TGA and DSC analysis and were related to the order degree of the coal structure as determined by the TEM, Raman spectroscopy and XRD. These results were published in two papers in International Journal of Coal Geology (App. 5, P2, P6).

Besides, I participated in studies on the influence of the addition of carbonized plant materials on the structure and physical properties of carbonized blends containing Zofiówka, Krupiński and Szczygłowice coals. As plant additives Yuka and bamboo pyrolysed under nitrogen at temperatures between 550 and 950 °C were used. My participation in this research, consisted in analysis of the viscoelastic properties of coal blends and their carbonization products. The research showed that big amount of functional groups and paramagnetic centers present in carbonized porous plants  significantly reduced the storage and loss modules of coal blends with their participation in comparison to the initial coal blends. The results of these studies were published in the International Journal of Coal Geology (App. 5, P4).

In 2010, I began cooperation with the Faculty of Chemistry of Rzeszów University of Technology in the frame of joint research work related to a subtask titled "Composite materials with increased strength and thermal resistance with the use of polymer resins for aerospace applications" as a component of the Key Project POIG 01.01.02-00-015/08-00 (App. 5, item II/H-7). My contribution involved the development and characterization of epoxy adhesive systems containing carbon nanofillers (carbon nanotubes and graphene nanofillers) for aviation applications that were characterized by electrical conductivity and met the requirements specified in this project. The results of this research were presented in the form of a report on the implementation of this subtask.

Since 2012, I have been involved in research on the use of anthracites as fillers in polymer-carbon composites. These studies were conducted initially under the research project of the National Science Centre No. 2012/05/B/ST5/00386 in a consortium with the Faculty of Chemistry at Rzeszów University of Technology (App. 5, item II/H-8). In this project, I participated as the principal contractor, project editor and person responsible for preparing reports. In the framework of the project, anthracite fillers with various graphene sheet order in their structures were obtained via pyrolysis of raw anthracite at high temperature from 950 to 2200 °C, and the structure and properties of these materials were characterized. Next, the composites with various anthracite fillers were obtained and characterized. There were found improved mechanical and thermal properties of the composites. First attempts to functionalize the well-ordered anthracite using oxidation methods followed by thermal reduction in order to separate graphene layers and to obtain

new layer-structured nanofillers were undertaken. The results of this research were presented at many national and international conferences (App. 5, item II/D-20, item II/J-10, J-11, J-12, item III/B-31, B-33, B-34, B-37, B-41-B-43, B-45-B-50) and published in indexed conference materials (App. 5, item II/A-14). Moreover, the publications in journals from the JCR list: Polymer Composites (H7) and Composites Part A (H6) were included in the scientific achievement.

Studies on application of natural carbon materials as fillers of polymer composites are still continuing and are focused mainly on functionalization of graphite and anthracite with a high structural order, using various chemical methods to obtain multi-layered graphenic nanofillers.

The cooperation with the Faculty of Chemistry from Rzeszów University of Technology is still continued and involves research on polymer, carbon and composite materials. Currently, joint research focuses on the use of anthracite materials with a graphite-like structure as a composite filler based on liquid crystal epoxy resins. The results of morphological observations and properties of the composite materials were used to prepare the manuscript titled "The influence of a magnetic field on the morphology and thermomechanical properties of a liquid crystalline epoxy carbon composite" published in Polymer Composites (App. 5, P13). This cooperative work is a continuation of the previous joint work on topics related to the effect of the cross-linking agent and addition of polyhedral oligomeric silsesquioxane filler on the viscoelastic properties of cross-linked crystalline epoxy resins with a central triaromatic mesogenic group. The results of this joint research were published in Macromolecular Symposia (App. 5, P5).

Since 2012, my research interests in carbon materials have been directed toward porous carbon materials such as carbon foams and glassy carbon, which are interesting fillers for polymer composites. The structure of these light materials, i.e., porosity, distribution and pore size, are strongly dependent on the type of precursor and the conditions of processing, which makes it possible to design their final properties. In addition to the results of research on using carbon foams as reinforcement of composites described in the postdoctoral thesis, I participate in the study of porous carbon materials (active carbons and carbon foams) obtained from other precursors than cross-linked polymer resins. These new precursors are primarily: coal pitches, petroleum products, polyolefins and polymer waste.

Since 2012 I have been a coordinator of a series of Polish-Bulgarian projects titled "Preparation and characterization of carbon materials from polymer by-products and wastes" (App. 5, item II/H-9, H-10, H-11). These projects were related to the preparation and characterization of porous carbon materials obtained from by-products in polyolefin production, primarily polyethylene waxes, and from recycled polyethylene terephthalate. In the frames of these projects, I participated in annual personal exchanges at the Institute of Organic Chemistry BAN in Sofia. In 2014 and 2015, I participated in the International Conference SGEM where I presented the results of these projects in the form of lectures and posters and chaired two poster sessions. The results obtained during these projects were presented at numerous national and international conferences (App. 5, item II/D-12,

D-14, item III/B-35, B-36, B-38, B-40, B-44, B-53, B-55) and published in the form of articles: Journal of Thermal Analysis and Calorimetry (H8), Composites Part A (H11) and Bulgarian Chemical Communications (App. 5, P9, P11, P12).

Since 2015, I have participated in a joint Polish-Ukrainian project on "Polymer composites with anthracite fillers as replacements for graphene/polymer composites" (App. 5, item II/H-12) in cooperation with the Institute of Macromolecular Chemistry of the National Academy of Sciences of Ukraine. In this project, I participated in work related to the chemical functionalization of anthracite materials towards graphene nanofillers and their use in the preparation of new polymer-carbon composites. The results of this research were presented in the form of oral and poster presentations at many national and international conferences (App. 5, item III / B-47, B-48, B-54, B-56, B-57) and were also published in the form of scientific articles in the journals Polymer Journal and .....( H10, H12).

I participate constantly in other work conducted at the CMPW PAN in Zabrze. In 2009, a cooperative venture associated with the use of thermal analysis was launched to characterize core-shell nanoparticles with a hyperbranched interior of poly(arylene-oxindole). My contribution relied on study of the thermal characteristics of star polymers of core-shell type consisting of arms of poly (tert-butyl acrylate) and a core of poly (arylene-oxindole) using differential scanning calorimetry and comparison with the properties obtained from characteristics of their linear counterparts. The common research results were described in the article in Journal of Polymer Science: Part A: Polymer Chemistry (App. 5, P3).

In 2012-2013, I participated in research related to solvent degradation of polylactide materials performed in Laboratory of Biodegradable Materials. I determined the effect of structure change of thin polylactide films due to aging and degradation processes in paraffin, glycerine and propylene glycol on their viscoelastic properties using dynamic mechanical analysis. The results from these observations and their interpretation were described in the article published in Polymer Degradation and Stability (App. 5, P7). This joint work is still continued, and the research focuses on the determination of the effect of 3D printing methods for plastic components manufactured from commercial polylactide and polylactide-polyhydroxyalkanes on their viscoelastic properties. Simultaneously, the study on the influence of hydrolytic degradation of these materials in abiotic conditions on the dynamic elastic modulus and glass transition temperature using dynamic mechanical analysis are carried out.

The work carried out in cooperation with the Laboratory of Membrane Materials and Processes concerned the determination of the effect of introduction of hexafluoroisopropylidene functional groups to amorphous poly(etherimides) chains . My contribution was to determine the dependence of the dynamic modulus of elasticity and glass transition temperature on the polymer structure. These research results were partially included in the paper published in 2013 in the Polymer Journal (App. 5, P8). Current research conducted as a continuation of this previous one addresses the influence of hydrophobic and hydrophilic zeolites on the molecular dynamics in the transition region

and the index of brittleness for membranes prepared from polysulfone and hydrogenated butadiene-nitrile rubber.

I participated in investigation of the crystallization processes of poly (2-isopropyl-2-oxazoline) (PIPOx) from aqueous solutions and from acetonitrile, dimethylsulfoxide and propylene carbonate in cooperation with Laboratory of Nano- and Microstructural Materials. Based on thermal effects of crystallization and thermal characteristics of products obtained using DSC method, the effect of the solvent and PIPOx concentration on the degree of crystallinity was determined. The results of this joint work were used to prepare the article published in 2015 in Macromolecules (App. 5, P10).

I work at the Institute of the Polish Academy of Sciences, and therefore, I do not conduct educational activities. However, I was responsible for substantive support during the implementation of two masters theses (P. Moryc in 2010, K. Olszowska in 2015). I led the experimental and measurement efforts during implementation of two master theses in the years 1999-2000. I was the auxiliary promoter of the doctoral dissertation realized in CMPW PAN and defended with distinction in October 2016 (App. 5, item III/K-1). The principal objectives of this thesis were epoxy composites containing anthracite fillers with various degrees of ordering of the graphene layers and nanocomposites containing a graphene-based nanofiller obtained via oxidative functionalization.

Furthermore, I continually supervised interns and trainees.

In summary, my scientific achievements consist of a total of **56** publications, including **28** articles published in journals indexed in the Journal Citation Reports list (JCR), **13** articles published in international and national journals outside the JCR database and **15** publications in conference materials of international conferences. The total Impact Factor of all publications according to the Web of Science database (WoS) is **50.878**, and according to the scoring list of scientific journals of Ministry of Science and Higher Education (MNiSW) from 2013, they are equivalent to **680** algorithm points. According to the Web of Science database, publications with my participation were cited **203** times, and the Hirsch index is **8**. According to Google Scholar, the number of citations of my works is **245**, and the Hirsch index is **9**. I took part or currently participate in **11** national and international research projects. I presented the results of my research at **48** scientific, national and international conferences, at which I gave **13** lectures (**4** national, **9** international). I was co-author of **16** oral presentations and **43** posters. I was also a reviewer of **70** scientific articles for the journals placed on the JCR list: Journal of Thermal Analysis and Calorimetry, Polymer Bulletin, Polymer Composites, Polymer-Plastics Technology and Engineering, Composites Part A, Polymer Testing, Journal of Industrial and Engineering Chemistry, Journal of Composite Materials, RSC Advances, Nanoscale Research Letters, Physica Status Solidi B, Journal of Alloys and Compounds, Advances in Polymer Technology, Express Polymer Letters and Materials Letters.Most of my scientific achievements were established in the period after I obtained a doctoral degree.