

CL-2-01 SIMULATION OF TEMPERATURE FIELDS IN CURING RUBBER

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Computation of temperatures in the heated and cured rubber is based on the Fourier equation of the transient temperature field. Important parameters in this equation are thermal diffusivity and reaction (curing) heat. Both of these quantities depend on the composition of rubber compounds but thermal diffusivity depends also on the temperature. Their values can be determined only experimentally. Because of a lack experimental data the curing process is often simulated with constant values of thermal diffusivities, and the influence of curing heat is ignored or in the better case estimated. Since the temperature fields depend on the instantaneous degree of curing equations of the curing model have to be solved simultaneously.

In order to simplify the mathematical model of rubber curing a new quantity called „effective thermal diffusivity“ is suggested. This quantity includes besides thermal diffusivity also curing heat. This allows to compute the temperature fields of curing in advance and then to calculate the fields of the curing degree from them. The determination of „effective thermal diffusivity“ has to be done at future technological conditions of rubber processing. In this case, the curing heat is not needed for modelling.

CL-2-02 PREPARATION AND PROPERTIES OF FERRITE POWDERS FOR RUBBER COMPOSITES

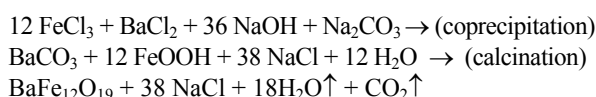
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The incorporation of magnetic polycrystalline ceramic ferrites in elastomeric matrixes produces flexible magnets or elastomeric magnets¹. Hexagonal ferrites with

magnetoplumbite structure have attracted the attention of researchers for a long time. The high values of magneto-crystalline anisotropy and saturation magnetization ensure a wide application of the M-phase ferrites as permanent magnets². Several methods have been developed to prepare ferrite particles and many efforts have been devoted to the development of synthesis procedures leading to a better control of particle size (<1µm), morphology (hexagonal plates) and homogeneity. The chemical co-precipitation method³ is a cheap and easy choice for mass production.

The aim of the study is to describe the details of co-precipitation synthesis of BaFe₁₂O₁₉ and detection of structural changes occurring during the synthesis process. It reports the results of an investigation of the morphological, structural and magnetic characteristics of BaFe₁₂O₁₉. Barium ferrite powders were prepared with molar ratio 2Fe/Ba = 5, 4 as follows:



The calcining temperature was changed from 800 to 1000 °C. It was found that the co-precipitation combined with high temperature results in M-type hexagonal powders whose particles are in the range (80–250 nm) in dependence of calcining temperature. From the TEM, FT-IR and Mössbauer spectroscopy results is evident that the increasing of the calcining temperature affects a decreasing amount of BaCO₃ and causes better formation of hexagonal plates in magnetic phase BaFe₁₂O₁₉ of resulted materials.

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CL-2-03 CARBON BLACK PRODUCED BY SCRAP TIRE PYROLYSIS

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The rubber samples (cca 200 mg) from a scrap tire were pyrolysed under atmospheric pressure and different temperatures. The carbon blacks produced (CB_{p1}) were

analyzed by the measurement of BET surface area (Nitrogen sorption method), pore structure (Nitrogen sorption method), iodine adsorption number (ASTM D1510), mass loss by heating at 125 °C (heating loss ASTM D1509), ash content (Thermogravimetric analysis) and pour density (ASTM D1513). The same parameters were estimated also for commercial carbon blacks N220, N330, N550 and N660. The third studied material was a pyrolytic carbon black produced by pyrolysis of scrap tire in an industrial scale batch reactor (CB_{p2}).

The parameters of the pyrolytic carbon black obtained in our laboratory (CB_{p1}) were compared with the parameters of commercial carbon blacks and also with the parameters of pyrolytic carbon black obtained in an industrial scale batch reactor (CB_{p2}).

Specific surface area of (CB_{p1}) has the values from 70 g m⁻² to 120 g m⁻² dependent on the pyrolysis temperature and type of the rubber material. Compared to the commercial carbon blacks these values correspond with the specific surface of carbon blacks N330 and N220. However, the CB_{p2} sample had a specific surface area comparable with N660.

The results of the measurements of iodine adsorption number have confirmed the similarity of CB_{p1} to N220 and CB_{p2} to N660. Pyrolytic carbon blacks had much higher ash content than the commercial one. Pour density of pyrolytic carbon blacks was also higher than pour density of commercial CBs.

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CL-2-04

RUBBER RECYCLING VIA HIGH-TEMPERATURE COMPRESSION MOULDING

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Rubber waste treatment is a great problem nowadays. Millions of waste tyres are produced worldwide per year. They are often trashed to landfills but this is both ecologi-

cally and economically unacceptable way. Regeneration of rubber is a common process but the utilization of its product is limited. Another way is to combust the tyres but only the energetical potential of rubber can be exploited in this case. To exploit the chemical one pyrolysis can be carried out. Another course is the material recycling. Waste rubber is ground and the product can be used as filler or it can be mixed with thermoplastics, liquid rubbers etc. A new material can be also obtained by compression moulding of ground rubber without any additive at high temperature and pressure¹. This paper focuses on the latter method.

Recycling possibilities of natural rubber (NR) and styrene-butadiene rubber (SBR) and their mixtures were tested on model compounds containing various curing systems. The model vulcanizates were ground and the crushed material was compression moulded at high temperatures (e.g. 250 °C) and pressure (20 MPa) to form a new material. Tensile properties, hardness, crosslink density and retention of these properties after thermal ageing were observed and compared to those of the original material. The real ground rubber from waste tyres was tested as well.

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CL-2-05

PHASE SELECTIVE DISTRIBUTION OF CARBON BLACK FILLED RUBBER BLENDS

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The phase selective carbon black distribution plays an important role regarding the performance of rubber composites based on rubber blends.

Since 2002 we use the online measured electrical conductance for the description of dispersion and distribution processes during the mixing process of carbon black filled rubber mixtures¹⁻⁴. Recently, we used this method also for the qualitative analysis of the morphology development of binary blends during the mixing process⁵.

With our new developed method, analyzing the carbon black-rubber-gel by thermogravimetric analysis (TGA) in correlation with differential thermo analysis (DTA) it is possible, to describe the wetting behavior of the polymer chains to the carbon black and the phase selective carbon black distribution during the mixing process. The determined carbon black distribution corresponds very well with the given carbon black distribution in blends of the masterbatches, and with results from the

online conductance measurements. With this method it is possible to characterize the free carbon black portion and the portion of carbon black in the particular blend phases depending on mixing time. In the present work we have investigated the effects of the material and technological parameters on the kinetic of CB distribution in SBR/NR blends by the use of the newly developed TGA/DTA method.

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CL-2-06

ADVANTAGES OF ACTIVE ZINC OXIDE'S APPLICATION IN RUBBER INDUSTRY

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Zinc oxide has showed to be the most important activator for sulphur vulcanisation of elastomers. In addition to its role as an activator, there are also evidences that the inclusion of ZnO in the vulcanizates brings also other benefits (it reduces heat-build-up, improves abrasion resistance, improves heat resistance of the vulcanizates and their resistance to the action of dynamic loading¹, helps to dissipate local heat concentrations in rubber products, it is necessary in vulcanizates for bonding rubber to the reinforcing steel cord, etc.). Besides improving the properties of vulcanised rubbers, ZnO also assists in the processing of uncured rubbers. ZnO is added to rubber formulations to decrease shrinkage of moulded rubber products and maintain the cleanliness of moulds.

Although zinc is generally considered as one of the least harmful of the heavy metals, there is an increased concern about its environmental effects². Diffuse emissions of zinc from rubber products, such as the wear of tyres may enter the environment. In view of the upcoming legislations and ecolabelling requirements for vehicle tyres, for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environmental but also for economical reasons^{3,4}.

This contribution tries to summarize the efforts how

to reach the above mentioned goal and presents some results from own research as well. The summarized results indicate that the same or better properties of vulcanizates can be reached by lower dosage of zinc oxide with higher specific surface.

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CL-2-07

CHARACTERIZATION OF THE FATIGUE BEHAVIOR OF ELASTOMER COMPOSITES

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In many engineering rubber applications both pure elastomeric materials as well as composites out of rubber and reinforcement materials, such as textile, polymer and steel cords, are used. Such technical rubber articles are often exposed to complex mechanical stresses, frequently in a cyclic mode, which can result in crack formation and crack propagation up to final failure of the relevant rubber article.

For example, air springs are used as structural damping elements in trucks, busses and in other heavy vehicles. The elastomer component in air springs typically consists of a multi-layer build-up, with an inner liner and outer cover of un-reinforced rubber and two fabric-ply layers containing polymer fibers of different orientations in a rubber matrix. To enhance the overall performance and life time of air springs, a more detailed understanding of the micro-mechanisms of failure under cyclic loads in such a multi-layer build-up is required. To support both mate-

rial development efforts and novel design concepts including life-time assessment, appropriate test methods and procedures to characterize crack initiation and crack growth resistance behaviour are needed.

In elastomer composites the following three basic micro-modes of failure have been identified for service relevant loading conditions: (i) crack formation and crack growth in the elastomer matrix, (ii) delamination between fabric-ply layers and (iii) crack initiation and crack growth at the cord (fiber)/matrix interface.

Hence, the main objectives of this paper are:

- The development and implementation of adequate test methods and data reduction schemes to characterize the crack initiation and growth resistance of multilayer elastomer composites under cyclic (fatigue) loading conditions including rubber matrix fatigue matrix/cord/fiber debonding and delamination of cross-ply layers.
- The application of the test methods to selected elastomer composite materials.

Several elastomer types and composite layer set-ups were included in the investigations. The materials were selected, manufactured and provided as test specimens by the company partner. The experimental work on test specimen level was performed in the testing laboratory of the scientific partner.

In the fatigue process of elastomers, at least two stages can be distinguished. The first stage is related to the crack nucleation and the initial phase of crack growth initiation, the second is concerned with the period over which the nucleated crack grows either in a stable or unstable manner until ultimate failure occurs. Current methodologies for describing elastomer fatigue behavior and to predict the service life of rubber components follow two general approaches. One approach focuses on predicting crack nucleation life and makes use of continuum mechanics parameters such as stress and strain. The other is based on fracture mechanics concepts and focuses on the kinetics of crack growth using energy based fracture mechanics parameters¹.

The fatigue behaviour of the bulk elastomer was characterized using a modification of the well-known pure shear specimen (faint-waist pure shear, FWPS) configuration and applying the tearing energy concept². Main emphasis was given to the characterization of the influence of preconditioning and processing parameters on the fatigue crack growth behaviour of elastomers used in real applications.

Furthermore, ring-type and peel-type specimens manufactured from cross ply laminates were used to characterize the fatigue behaviour of the elastomer composite layers. While due to the high local stiffness difference between the rubber and the cross-ply the main load for the ply interface is near mode II (shear stress) in the ring specimen, the peel test represents the mode I (opening) loading situation. A complex combination of these two basic modes may occur in a real component during service. Moreover, a novel test set-up for characterizing the

rubber matrix/cord interface under cyclic loading was also developed and implemented.

Finally, component tests were also performed. In addition to the conventional tests, novel full-field strain analysis methods were applied to characterize the strain and temperature distribution in the component under complex cyclic loading conditions. To gain more insight into the local failure behaviour, failure analysis on both test specimen and component level was carried out using various microscopy methods.

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CL-2-08

WEAR OF RUBBER COMPONENTS

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Polymer processing industry is a very branched one because of the production of a lot of products for various applications. Products from polymers and composites with polymer matrix find wide use: products for common use, sports and free time activities, domestic goods, packaging, medical applications, construction, electrotechnics and electronics, engineering and automotive industry. Rubber industry plays a very important role in the polymer processing since the tire production occupies a dominant position in this branch.

The tire is a very important part of the vehicle which is in direct contact with the road surface and responsible for the driving force transfer. In terms of design, tire is a very complicated component consisting of polymeric matrix and reinforcement. It is composed of various layers. In terms of wear, the overlayer called tread equipped with design (pattern) is the most important part.

The wear of tire treads on road surfaces is measured as abrasion resistance. The off-road behaviour of tyre treads on surfaces with sharp stones is not well character-



Fig. 1. Sample before and after test



Fig. 2. Sample wearing during test period

ised by abrasion resistance as the mechanism of rubber damage is rather different here. The sharp edges of stones can cut rubber tread surfaces and tear off bigger pieces of rubber gradually. This type of wear is called chip and chunk effect in the tire processing industry and with a simplification, it is comparable to machining.

The tire wear is usually tested under running conditions, and these long-lasting tests are very expensive. Finding a fast test carried out on small samples would be very useful in practice.

The test for cutting and chipping of rubber compounds which correlates with service behaviour and provides test results at a reasonable speed and accuracy was described by J. R. Beatty and B. J. Miksch¹. In accordance with their description we constructed a rather modified apparatus.

The tests were carried out on cylindrical samples of the Lüpke test with diameter 55 mm and thickness 13 mm (Fig. 1, ref.³).

This enhanced laboratory apparatus provides to take test of conditions which can be widely changed. It makes possible to measure different characteristics of chip-chunk processes.

Thirteen various types of tire tread mixtures designed for off-road tires production have been chosen for the experiments (motocross and multipurpose tires).

The presented test method shows the possibility of the evaluation of wear (chip-chunk) resistance of tire treads on small samples. This method makes possible to compare various types of compound with a standard and to observe the wear progress during the test period. The wear of the sample during the test period depends on the properties of rubber compounds and on test conditions. A significant correlation of chip-chunk resistance with the usual rubber properties was found (Fig. 2). According to the statistical calculation all the measured data are statistically significant².

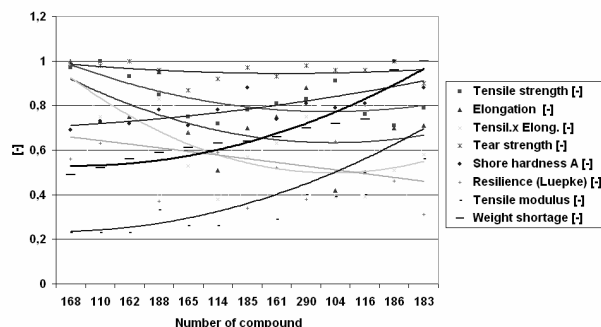


Fig. 3. Comparison all measured properties

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CL-2-09

EFFECT OF FILLING DEGREE IN TWIN SCREW EXTRUDER ON CONTINUOUS COMPOUNDING OF E-SBR/SILANIZED SILICA COMPOUND

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The paper focuses on experimental investigations of the continuous mixing of a silica filled rubber mixture with a co-rotating twin screw extruder. The rubber mixture is a free flowing Rubber/Filler Composite (RFC) based on emulsion styrene butadiene rubber (E-SBR) with silanized silica as filler. The reaction between the silica and silane is carried out during the production process of RFC and hence the rubber mixture contains completely silanized silica¹. Continuous mixing involves compounding all the ingredients together in one mixing step. The continuous mixing of silanized silica based rubber mixture requires

optimum process parameters to assure micro-dispersion². This property influences the dynamic shear modulus value at low strain measured with a rubber process analyser (RPA) which influences the Mooney viscosity of the final compound. In the experimental work, the influence of filling degree in twin screw extruder with respect to screw speed and output on the compound and product properties are analysed. The mixture characteristics shows that filler dispersion and cross-linking behaviour and the properties of the vulcanised rubber correspond to the characteristics of the reference compound mixed in the internal mixer.

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CL-2-10 INFLUENCE OF SURFACE QUALITY ON FLUIDITY OF ELASTOMERS

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This paper shows influence of technological parameters on the flow length into mold cavity. The fluidity of elastomers is affected by many parameters (mold design, melt temperature, injection rate, pressure and curing process).

To be able to study the influence of surface quality of runners and cavities on the flow of elastomers, a special injection mold has been designed and machined. Injection

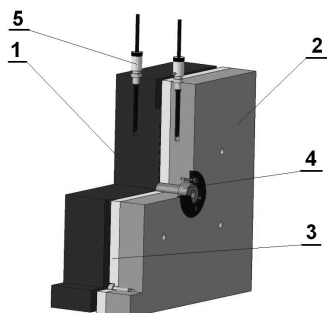


Fig. 1. Injection mold

Table I
Values of surface quality of testing plates

Polished plate	Ra=0,029 μm
Ground plate	Ra=0,369 μm
Electroerosion machined plate (“fine”)	Ra=3,520 μm
Milled plate	Ra=9,368 μm
Electroerosion machined plate (“rough”)	Ra=17,393 μm

mold is assembled from (1) cavity plate, (2) clamping plate, (3) testing plate, (4) sprue bushing, (5) temperature sensor (Fig. 1).

The surface of the plates (bottom of spiral) is machined using various types of working technologies: milling, grinding, polishing and electro-spark cutting.

Length of testing samples has been measured by measuring jig. The experimental dates have been statistical processed and evaluated. Injected samples were prepared on injection molding machine REP V27/Y125.

For preparing of injected samples were chosen three rubber compounds with different flow properties. These compounds have to have sufficient processing safety

Table II
Injected rubber compounds

	Hardness [ShA]	Strength [MPa]	Elongation [%]	Viscosity (1+4 min/100 °C) [°MU]
A	50±5	10	300	31
B	60±5	7	250	40
C	65±5	16	300	73

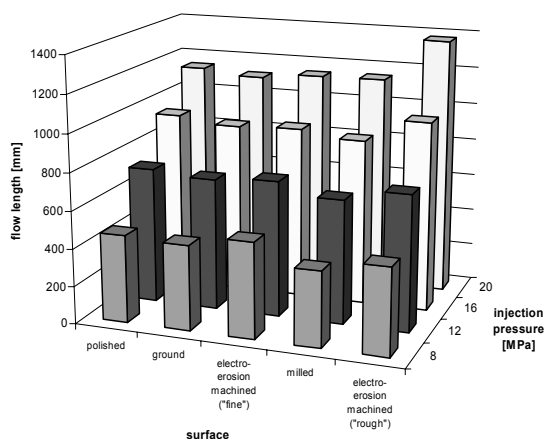


Fig. 2. Dependence of flow length on surface quality and injection pressure (compound A)

(scorch safety) to flow through the nozzle, runners, and gates without scorching, but still cure rapidly in the mold.

Measurement shows that surface quality doesn't have substantial influence on the length of flow. Samples which were injected into the spiral (cavity) with the worst surface quality have approximately same length of flow in comparing with the best surface fluidity. These findings are very important from the point of view of use in production. For verification of these results further experiments have to be carried out using different rubber compounds.

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CL-2-11

SIMULATION OF DEFORMATION BEHAVIOR OF REINFORCED RUBBER BY A NETWORK MODEL COMBINED WITH FEM

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A modeling of deformation properties of rubbery material was presented in this contribution. This model was designed to description and prediction of mechanical properties from its structure and material properties. The progress from simple network model (NM)¹ to the model of real polymer material was presented. In the first approximation, the model was a 3D tetra-functional network of rubbery matrix², in which undeformable inclusions were introduced. This network model was approached to the behaviour of real polymer material. First, the NM was combined with Finite Element Method (FEM). By the FEM, the distribution of deformation and stresses during the tensile test was analyzed.

In the second phase, the structural properties approached to the real behaviour of the rubbery material. Before, the network was fully affine. The chains were fixed in the nod. Then a portion of chains was replaced by so called free entanglements. Both fixed nod and entangle-

ments were permanent nodes. That means that they did not disappear or re-appear during the virtual tensile test. The entanglement enabled slipping of the chain through the nodes of the network. The third variant of a node was a tie-point. This node was unstable and it disappeared during the tensile test. Each variant of node represented certain component in the structure of polymer. The fixed node represented for example Sulfur Bridge, the free entanglement the entangled chains and the tie point represented two polymer chains adhered together by weak intermolecular forces.

Virtual tensile tests were performed on the homogeneous rubbery networks and composite networks with undeformable inclusions. The stress/ strain curves until five fold elongation of sample were calculated. Some material characteristics were derived from the curves such as Young modulus, stress at break. The loading-unloading curves were calculated until the double elongation. Mainly heterogeneous materials show nonlinearly elastic deformation response³. The energy dissipated during one loading-unloading cycle was calculated by the model.

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CL-2-12

MOLECULAR CHARACTERIZATION OF SYNTHETIC POLYMERS BY SIZE EXCLUSION CHROMATOGRAPHY

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Molecular characteristics of polymers – their molar mass, chemical structure (composition, functionality, etc.) and physical architecture (linearity, branching, stereoregularity, cis-trans isomery, etc.) – both average values and distributions co-determine the end-use properties of corresponding plastics and rubbers. Presently, size exclusion chromatography (SEC) called often also gel permeation chromatography dominates the field of molecular characterization of synthetic polymers. Besides the molar mass averages and distributions, SEC provides useful information also on the long chain branching of macromolecules, on intrinsic viscosities and gyration radii of dissolved polymer species, as well as on preferential solvation of

macromolecules in mixed solvents. Important products of SEC include also data on association, aggregation and micellization of macromolecules. SEC is fast, relatively cheap and it exhibits rather high inter-laboratory repeatability (precision). Measurements, including sample preparation are usually not labor-intensive and sample consumption is low. Based on (universal) calibration or in combination with the flow-through light scattering or viscometric detectors, as well as with ultraviolet, infrared and mass spectrometries, SEC can provide valuable additional information about numerous soluble polymer species. Modern automated and often robotized fast SEC instruments have reduced time of analysis down to few minutes so that some polymerization processes can be on-line monitored and optimized.

At the same time, however, SEC suffers from numerous shortages. Recent series of round robin tests demonstrated surprisingly low accuracy (low inter-laboratory reproducibility) of SEC data obtained without strict protocol of both measurements and data processing. It is evident that a worldwide standardization is necessary of practical measurements (for example in terms of sample preparation, as well as of its volume and concentration), and data acquisition/calculation (for example in terms of base line and peak limit setting). The analysis of above round robin tests results clearly shows that expertise is needed for accurate SEC measurements. The approach „switch-on, inject, switch-out; computer itself and without inspection will produce SOME data“, which is often applied in many universities and research institutions, may produce results differing several hundred percent from the median values. It is anticipated that the high-speed, high sample throughput SEC procedures are especially susceptible to large errors.

The intrinsic though often overlooked or ignored shortages of SEC include: low selectivity of SEC separation and imperfect column „linearity“, dependence of polymer retention volume on both sample concentration and volume, low sensitivity and selectivity of detectors,

limited solubility of some polymers so that high temperature measurements or expensive eluents are needed, as well as broadening of chromatographic zones. Unavailability of the calibration standards is usually overcome applying calibration with polystyrene standards. Molar masses obtained in the latter way, however, represent only relative data and should be denoted „polystyrene-equivalent values“. Important problems of SEC are caused by presence of the non-controlled enthalpic interactions between separated macromolecules and column packing, which result in shifts of sample retention volumes. Effects of enthalpic interactions are partially but often not fully suppressed by using light scattering or viscometric detectors. SEC also suffers from the low sample capacity of columns, which are easily overloaded and resulting SEC peaks are extensively broadened or deformed. This is why the minor macromolecular admixtures (1 % and less) in polymer samples cannot be directly characterized by SEC – even if their molar masses well differ from the molar mass of the major component. Possible changes of sizes of macromolecules during SEC measurements represent further shortage of SEC. The latter are caused by the (de)association, (de)aggregation or degradation of polymers species within column. The flow induced shearing leads to mechanical degradation of macromolecules with molar masses over one million and especially over ten million of g mol^{-1} . Large column packing particles and low flow rates must be applied for ultra-high molar mass polymers. Large column packing particles, however, bring about increased band broadening phenomenon.

Selected shortages of size exclusion chromatography, especially effects of un-controlled enthalpic interactions within the SEC columns will be discussed in this contribution.

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