

Composite materials with photo-responsive capability

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Doctoral Thesis Summary



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Composite materials with photo-responsive capability

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ABSTRACT

Photo-responsive materials belong among novel, fast-developing intelligent materials of modern era. They seem to be promising smart systems in many current and future technologies i.e. in medicine, mechanical and construction engineering, energy harvesting, sensors etc. Very encouraging group of these materials is represented by photo-actuating (PA), shape-memory systems. Their main feature known as photo-actuation is capability to rapidly and reversibly change their shape after external light exposure.

However, there are several limitations reducing their real-life utilization. Generally known PA systems, mainly solid materials, suffer from not very significant dimension change that is usually in order of 0.001% of original shape. Hence, the main aim of this work is focused on composite systems, in which the combined PA effect of matrix and filler is frequently synergic, but those systems also possess many drawbacks that need to be solved, i.e. low compatibility of filler to the matrix related poor dispersibility in such system resulting to the low thermal conductivity and finally poor mechanical properties as well as PA capabilities. The mentioned drawbacks can be reduced by modifying the filler with compact polymer layer possessing such surface properties those can significantly enhance particle/matrix compatibility and thus contribute to considerably improve overall properties.

ABSTRAKT

Fotocitlivé materiály patří mezi nové, rychle se rozvíjející inteligentní materiály moderní doby. Ukazují se být slibnými inteligentními systémy, které lze využít v mnoha současných a budoucích technologiích v oblastech jako jsou medicína, strojírenství, stavebnictví, získávání energie, senzorech a dalších. Velmi nadějnou skupinou těchto materiálů jsou foto-aktuující systémy s tvarovou pamětí. Jejich hlavní funkcí známou pod pojmem foto-aktuace, je schopnost rychle a reverzibilně měnit svůj tvar po vystavení se vnějšímu světelnému stimulu.

Jejich reálné využití v praxi se potýká s několika omezeními. Obecně známe foto-aktuující systémy, zejména pak pevné materiály, nevykazují významnou změnu jejich rozměru, ta se obvykle pohybuje řádově 0.001% původní velikosti. Proto je hlavní cíl této práce zaměřen na kompozitní systémy, kde kombinace matrice i plniva, které mají schopnost foto-aktuace, má synergický efekt. Nicméně, tyto systémy mají řadu nevýhod, které je třeba vyřešit. Nízká kompatibilita plniva s matricí způsobuje nedostatečnou disperzi částic v takovémto systému, což vede k nízké tepelné vodivosti a finálně ke špatným mechanickým vlastnostem, stejně tak k nedostatečným foto-aktuacím schopnostem. Zmíněné nevýhody mohou být eliminovány modifikací plniva kompaktní polymerní vrstvou, která má takové povrchové vlastnosti, které mohou významně zvýšit kompatibilitu plniva s matricí, a tak přispět k podstatnému zlepšení celkových vlastností.

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1 THEORETICAL BACKGROUND

1.1 Introduction

The intelligent materials have its place in increasingly evolving areas of material science and engineering. The external stimulus-responsive materials are of attention for many scientific researchers, due to their capability of reversibly change their dimension upon the application of an outside stimulus i.e. electric [1] and magnetic [2] field, temperature [3], pH [4], light (UV, VIS), etc. [5]

Actuators provide the driving force and motion for a variety of natural and manmade requirements. Naturally, occurring actuators include the muscles of animals and plants, and manufactured actuators include hydraulics [6], pneumatics [7] and solenoids [8]. Other fabricated actuators, such as piezoelectric [9], shape memory alloy [10] and magnetostrictive [11] devices, are based on shape-changing materials; these are used increasingly in novel applications. Actuators offer a wide variety of performance and operate in many different ways.[12]

Light-induced actuators are attractive to scientists since they propose an effective means to couple light energy into the actuator configurations, and bring advantages of basic systems with wireless functionality, remote control, green energy, and high-level integration [13, 14]. The effect of the Photo-induced Optical Anisotropy (POA) is a phenomenon that was observed in many molecular systems such as solutions [15], polycrystalline films [16], polymer films [17] and Langmuir-Blodgett (LB) films [18, 19]. The photomechanical actuators (also known as photo-actuators) are a class of smart materials that can alter their dimensions or undergo mechanical motion when exposed to photons (light emission) [20]. Absorption of the energy from photons leads to a contract or a generation of a certain mechanical motion of polymeric chains, which is called photo-actuation. [21-23]

Graham Bell firstly used a concept of so-called photo-actuation in 1881. He used the opto-acoustic effect to make sound in a gas with chopped beam of sun light that has been used to study the absorption of light by materials throughout the next 100 years. [24] An optically operated fluidic actuator was presented in 1980 [25]. In 1983, the optical heating of closed gas filled volume was used to change a flexible diaphragm in a flapper nozzle device [26]. In 1990, the first direct optical to mechanical actuation was achieved by optically modifying the viscosity of a fluid[27]. The rapid development in materials research in the early 1990's led to the expansion of range of photomechanical actuators based on direct and indirect optical to mechanical energy conversion [26].

This thesis aims to develop such photo-actuator in form of composite, which combines photo-actuation properties of matrix and filler to produce such shape-change material that will rapidly exceed dimension change of individual components.

1.2 Mechanisms of photo-actuation

Materials that can reversibly change their physical properties upon application of external stimuli are used as actuators for robotics, optical switches, optical displays, prosthetic devices, micro pumps, computer accessories, automotive sensors, and interplanetary space missions. The best-known materials used today for actuation are piezo-electrics, ferro-electrics, shape-memory alloys, electro-restrictive materials and conducting polymers. However, the maximum allowable operation temperature, the need for high voltages, and the limitations on the work density per cycle restrict applications of these materials [26]. The phenomenon of photo-induced strain has been previously observed in lead zirconate titanate (PLZT) ceramics [28], polymers [5], nematic elastomers [29], polarizable liquids [30] and chalcogenide glasses [31].

1.2.1 Polymers

The most common principle of photo-actuation of chemically cross-linked elastomers and/or TPEs is based on the presence of soft segments responsible for shape changes under illumination, and hard segments responsible for returning the material to its stage before illumination. Thus, the pre-strained material containing some light absorbers absorbs the energy from the light and converts it to heat that is conducted through the material [32]. The heat causes that the pre-strained polymer chains in the soft segments shrink, i.e., contract to form coil, and that results in shape changes of the material [33], as can be seen in Figure 1.

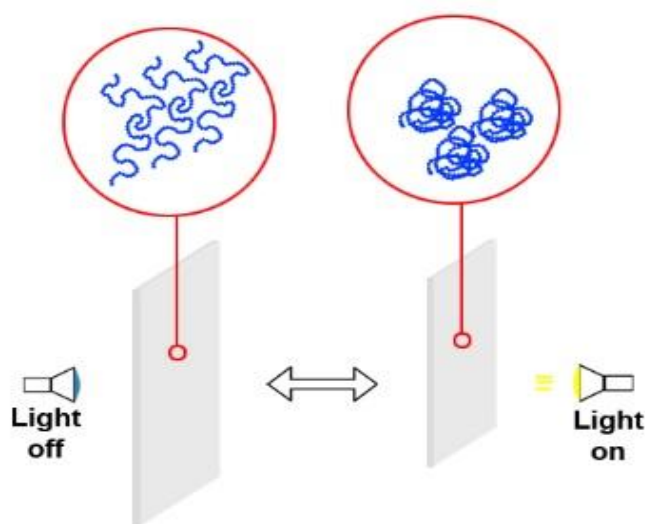


Figure 1. Photo-actuation of polymers [34].

1.2.2 Nematics elastomers

Photo-anisotropic materials are widely investigated for optical storage and processing applications. The most promising of them seem to be azo-dye-polymer systems because of the large value of the photo-induced birefringence in them

[35]. Photo-actuation in azobenzene polymers are caused due to the optical switching of the polymeric material from cis (contraction) to trans (expansion) isomeric states of the polymeric material. Actuation occurs in the UV region between 260–300 nm wavelengths. [36, 37] Liquid-crystalline polymers (LCPs) are one of the representative actuating materials. When liquid-crystalline monomers are polymerized in the nematic phase, they form liquid-crystalline polymer networks with aligned molecular structures. Incorporating azobenzene into an LCP system yields an azobenzene-functionalized liquid-crystalline densely cross-linked polymer (azo-LCP) system, which can convert UV or blue-light irradiation into mechanical deformations [38].

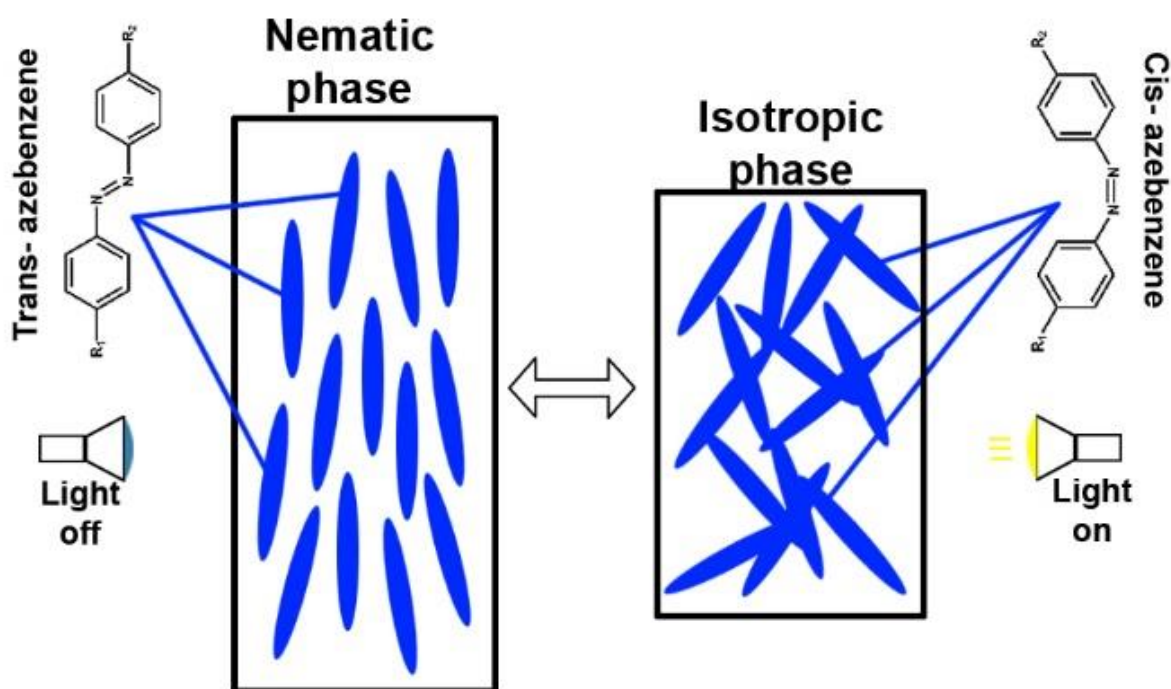


Figure 2. Photo-actuation of nematic elastomers [39].

1.2.3 Ceramics

Photo-actuation in PLZT ceramics is triggered by the superposition of photovoltaic effects, and the converse piezoelectric effect. It arises only in resources which are non-centro symmetric (typically piezo and ferro-electric). The large photo-voltage that is produced, reasons to the expansion or contraction of the frame in the way of unprompted polarization of the material and is reliant on impurity doping and crystal asymmetry. Such effects have practical application in creation micro-mechanisms, photo-relays and wireless actuators. The change in dimension reached by the PLZT materials does not exceed ~0,1% and is comparable to piezoceramics [23].

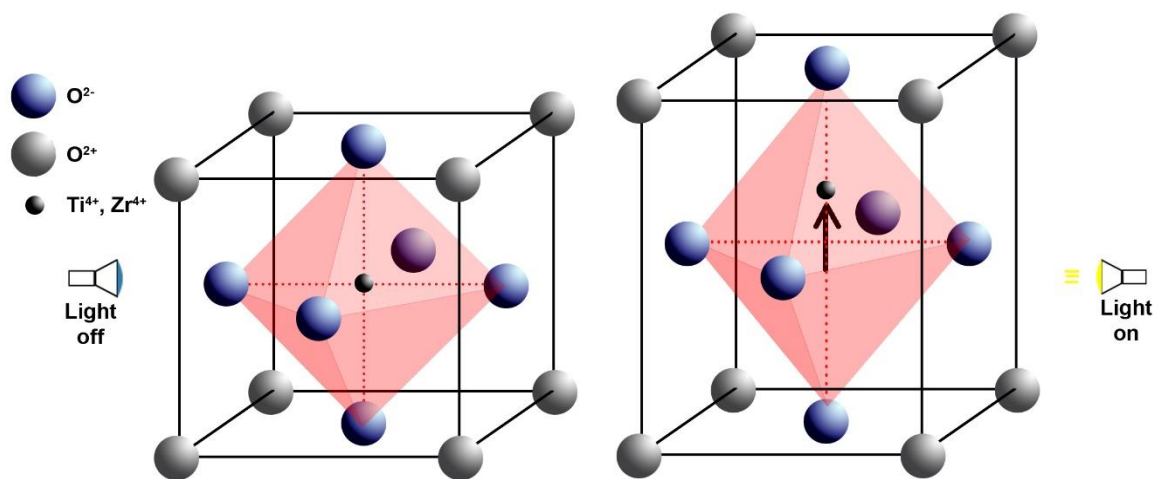


Figure 3. Photo-actuation of ceramics [40].

1.2.4 Chalcogenide glasses

More recently, chalcogenide glasses have been observed to directly convert light into mechanical energy. The investigations showed that upon irradiation with polarized light, thin film of chalcogenide glasses exhibit reversible nano-contraction parallel to the direction of the electric vector of the polarized light and nano-dilation along the axis orthogonal to the electric vector of the light. This new actuator technology shows promise of using polarized light for actuation that is scalable using massively parallel manufacturing techniques. However, the kinetics for contraction and relaxation are in the range of 1 min to 2 min making this actuation slow and the strains achieved are small ($<0.001\%$). The range of actuation is also within nanometers, which have to be extended to micro and millimeters for more practical applications in MEMS and macro-scale actuation technologies. [26, 41-51]

1.2.5 Composites

Previously mentioned materials have different ability to change their shape after using light stimuli on them. The enhancement of their performance requires to increase their rubbery modulus and to minimize strain-recovery after deformation while maintaining processability, durability, deformability and to perform many cycles by means of repeatability [52]. In addition, there is an increased activity in integrating those materials with nanotechnology to prepare new materials for the realistic applications. Composites filled with neat particles and/or modified particles develop the photo-actuation phenomenon and may provide additional impact on the mechanical properties of the final composite system, which considerably influence the final photo-actuation performance.

1.3 Composition of Photo-actuating systems

Generally, the actuating materials can be pure polymers or polymer composites, but they need to have the energy absorber that serves as a trigger to actuation.

That is why usual photo-actuator is consisting of two main phases. Usually filler, which is kind of energy absorber that is dispersed in elastomeric matrix. Various elastomers were investigated for their photo-actuation behavior, including liquid crystalline elastomers [53], poly(dimethylsiloxane) (PDMS) [54], different thermoplastic elastomers based on polyurethane [55], poly(ethylene-co-vinyl acetate) (EVA) [56], polystyrene-block-polyisoprene-block-polystyrene (SIS) [57], and acrylic-based block copolymers, as well as hydrophilic copolymers such as NAFION [58] or hydrogels based on copolymers of acrylic acid and N-isopropyl acrylamide [33].

1.3.1 Matrix

1.3.1.1 Chemically cross-linked elastomers

Chemically cross-linked elastomers have the characteristics of rubber in terms of their flexibility and elasticity. The long, randomly coiled, loosely cross-linked materials can be stretched easily and they return to their original shapes when the force or stress is removed [59]. Most commonly used materials are liquid crystals and PDMS, because they provide good actuation behavior [60]. Because of the structure of LCs, by integration of the light-triggered materials to the LCs, the alignment can be controlled over large parts, and hence the materials can be effectively applied in photonic applications such as photo-actuation [33].

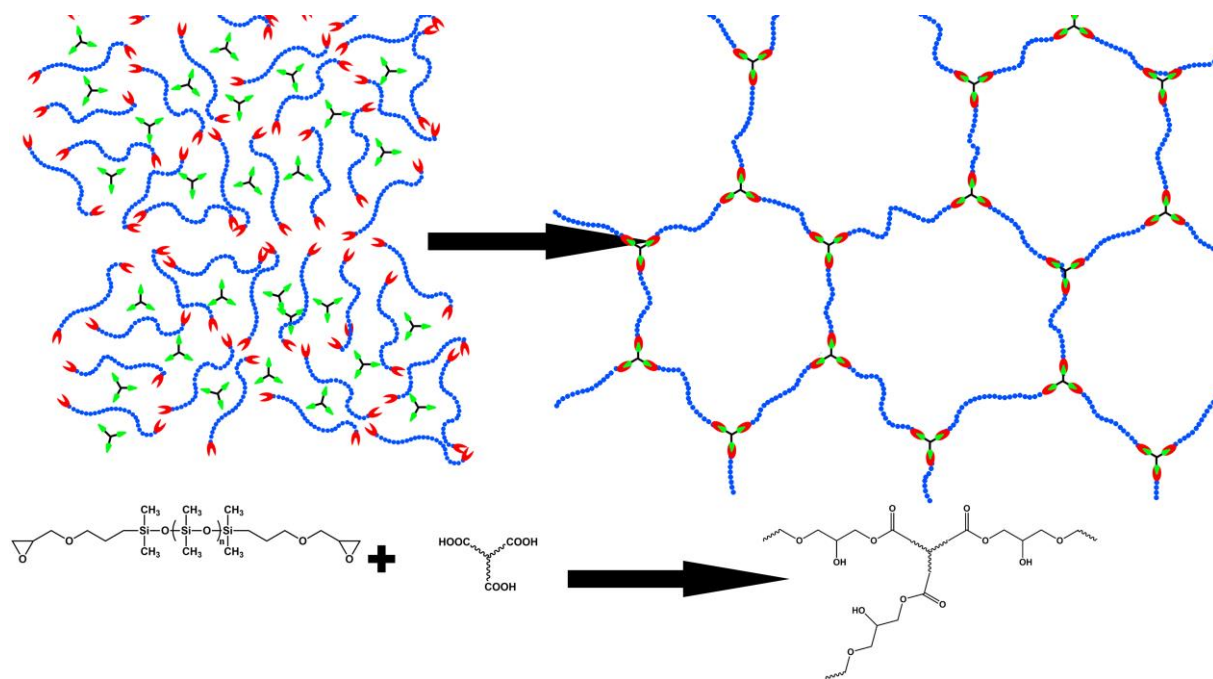


Figure 4. Chemical cross-linking of poly(dimethyl siloxane) [61].

1.3.1.2 Physically cross-linked elastomers

Physically cross-linked structure have several benefits in contrast with chemically cross-linked elastomers. The repeatable processing by large-scale techniques and potentiality of tuning mechanical properties are their main advantages. They are also cheap in comparison to LCs and PDMS. They are very

promising in terms of large-scale industrial use. Physical cross-linking can be acquired by absorption of chains onto the surface of finely dispersed fillers, formation of small crystallites, coalescence of ionic centers and coalescence of glassy blocks [62]. Such obtained materials are part of group of polymers, called thermoplastic elastomers (TPE). Most TPE are phase separated systems. One phase is usually hard and solid at laboratory temperature and other is an elastomer [63]. TPEs can be divided into seven currently known groups: Styrenic block copolymers [64], crystalline multiblock copolymers [65], miscellaneous block copolymers, combinations of hard polymer/elastomer [62], hard polymer/elastomer graft copolymers, ionomers [66] and polymers with core-shell morphologies [67].

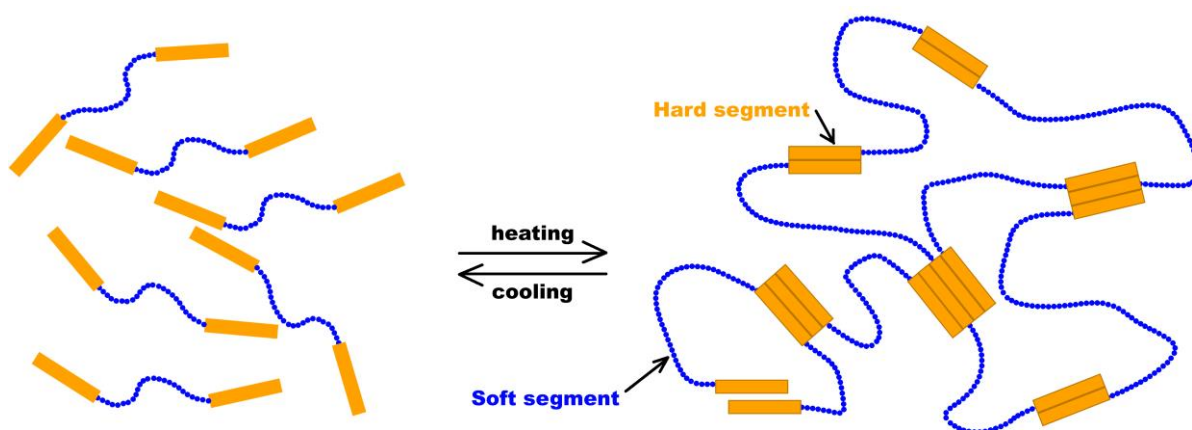


Figure 5. Physical cross-linking of thermoplastic elastomer [68].

1.3.2 Fillers

1.3.2.1 Organic fillers

As an organic filler, the azobenzene moieties in the main chains polymer films are used. Visible light facilitated the photo-isomerization of azobenzene moieties with directly modified cores or added substituents in LCPs [69]. Triplet-triplet annihilation-based up conversion luminescence materials were used to convert red light at 635 nm into short wavelength light, indirectly stimulating the prepared cross-linked LCPs containing azotolane [70].

1.3.2.2 Carbon-based fillers

Carbon nanotubes (CNT) based composites provide remarkable mechanical properties with very high elastic modulus and electrical conductivity [71]. CNTs can serve as photo-actuators due to the electrostatic interaction between the CNT bundles caused by light-induced thermoelectric (or photovoltaic) effects [72]. However, such photo-actuators are limited by the small mechanical deformations [73]. Carbon nanofibers have the potential to be used in nano-electronic devices, such as in artificial muscles, as well as in electrochemical energy storage matrices. Carbon-based nanoparticles like GO show the enhanced thermal conductivity and storage modulus, while the glass transition temperature is slightly decreased [74].

In practical applications, the conductive PA systems may be used as strain sensors based on the relation between electrical conductivity and strain.

1.4 Crucial parameters of photo-actuating systems

From information mentioned above, the crucial parameters are depending on used matrix and filler. Size, shape and dispersion are limits of filler, which affect final PA performance. In case of the size, fillers can be nano or micro sized. Advantages of nanoparticles are their high aspect ratio, large surface area; superior mechanical and thermal properties [75] on the other hand micro particles dimension shape-change is higher, due to the generally better and more homogenous dispergation in polymer matrix in comparison to nanoscale filler those form aggregates in there is not performed surface modification. In this consequence, the thermal energy redistribution in the sample is a crucial factor for the final photo-actuation and is better for the systems with homogenous filler distribution than for system with local inhomogenities formed by aggregates. In the case of matrix, the most crucial parameter is flexibility. The more flexible system is, the higher the PA performance can be achieved.

1.5 General characterization of materials

1.5.1 Dynamic mechanical behavior

The most precise tool for the photo-actuation investigation is dynamic mechanical analysis (DMA) in iso-strain tensile mode. Dynamic mechanical properties are ones of the most crucial factors influencing the applicability of materials as photo-actuation systems. Reversible contraction/elongation of the sample by light stimulation is a rather dynamic process and, therefore, investigation upon dynamic conditions is very important. Obtained data allow the calculation of the complex modulus in Equation (1) (knowing storage and loss moduli), damping or tan delta, δ , as well as viscosity data. The dynamic mechanical properties of a polymer are described in terms of a complex dynamic modulus [71]:

$$E = E' + iE'' \quad (1)$$

where E' is the storage modulus and is a measure of the recoverable strain energy, when deformation is small, it is approximately equal to the Young's modulus. E'' means the loss modulus and is related to the energy dissipation. DMA allows the rapid scanning of the viscoelastic moduli of composites as a function of temperature or frequency [71]. In addition, DMA is very sensitive to the motion of polymer chains and, therefore, they are powerful tools for measuring the glass transitions in polymer matrix. Moreover, the proper incorporation of the filler to polymer matrix can be estimated using Arrhenius equation (2) a can be quantified using calculation of pseudo-activation energy E_a .

$$\ln f = \ln f_0 - \frac{E_a}{RT_g} \quad (2)$$

Where f is the tested frequency, f_0 is the constant characteristic of material, T_g is the glass transition temperature and R is the universal gas constant.

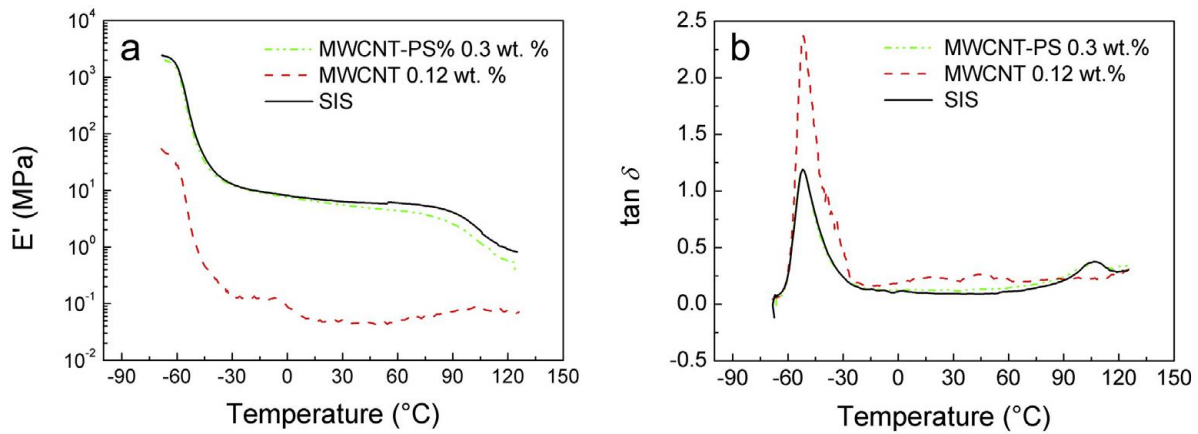


Figure 6. Temperature dependence of a) elastic modulus and b) $\tan \delta$ of composite [57].

1.5.2 Dielectric properties

Dielectric properties are very often used as tools for investigation of polymer chain dynamics.

Investigation of dielectric properties is very important because with the help of measurement in a broad temperature range and frequency-dependent permittivity it is possible to calculate E_a of the glass transition and T_g , which provides information about the polymer chain flexibility in the presence of particles. The flexibility of the polymer matrix is given by two factors, the mobility of the main chain characterized by an α relaxation, corresponding to T_g , and the side chains mobility characterized by α' relaxation, indicating how the entanglements of the side chains got stiff. Therefore, both relaxations are investigated using the Arrhenius equation (3) [76].

$$\tau = \tau_0 \frac{E_a}{kT} \quad (3)$$

Where τ is relaxation time, τ_0 is pre-exponential factor, E_a is activation energy, k is Boltzmann constant, T is temperature [77].

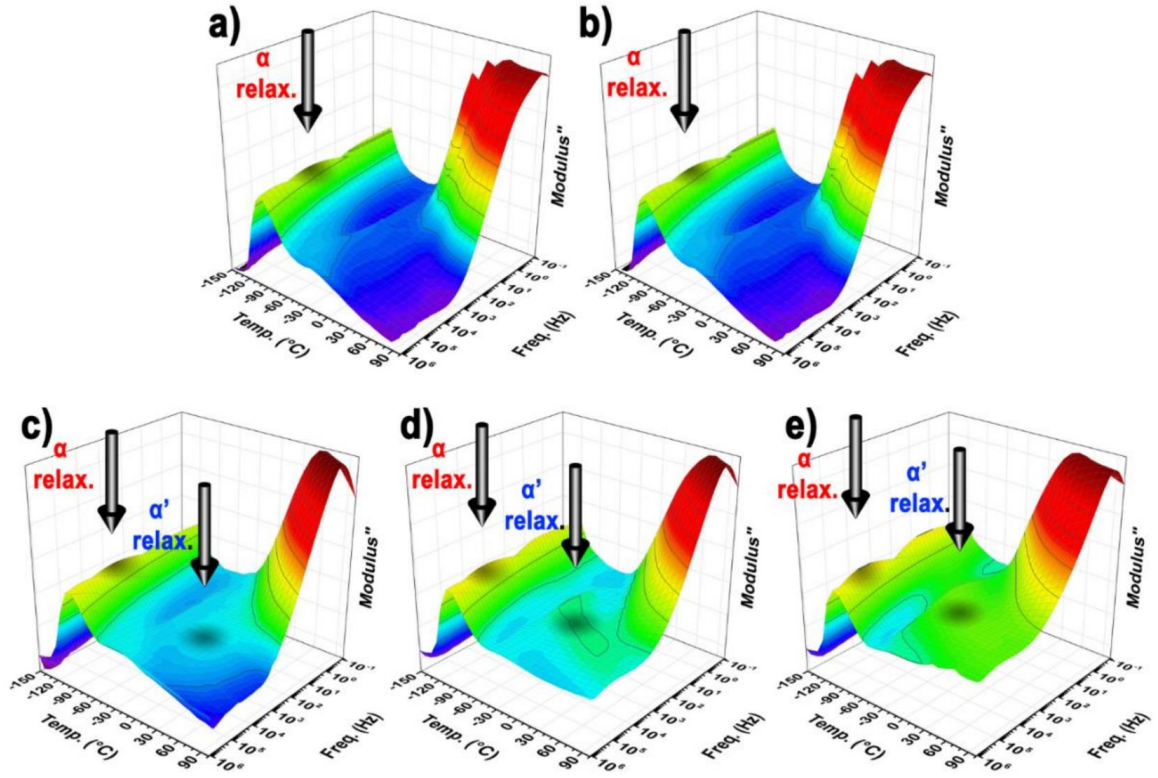


Figure 7. 3D plots of the dielectric properties of the neat PDMS matrix (a), and PDMS matrix filled with GO [76].

In order to appropriately study, the polymer chains dynamics, the loss permittivity desired to be recalculated to the loss modulus. This recalculation is achieved according to equation (4, 5, 6).

$$M^* = \frac{1}{\varepsilon^*} \quad (4)$$

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad (5)$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (6)$$

where ε^* is the complex permittivity, ε' and ε'' are relative permittivity and loss permittivity, respectively. M^* , M' and M'' are complex, storage, and loss dielectric moduli, respectively.

Then the activation energies are calculated to show flexibility of the matrix, the lower activation energy system possess, the lower energy is needed for its actuation.

1.5.3 Viscoelastic properties

Due to their exceptional conformation, the PA systems show complicated flow characteristics, which are essential to be determined in order to evaluate their suitability in practical application. To evaluate suitable compatibility of the matrix and filler the rotational rheology mainly in case of TPEs is used [78]. From the position of the crossover point is able to determine whether the filler was properly

mixed into matrix and the particles are well-dispersed through the composite [79]. The viscoelastic properties of the matrix and nanocomposite are investigated in oscillatory shear mode. The values of G' and G'' shows the interactions between the matrix polymer chains and the filler as is shown in Figure 8.

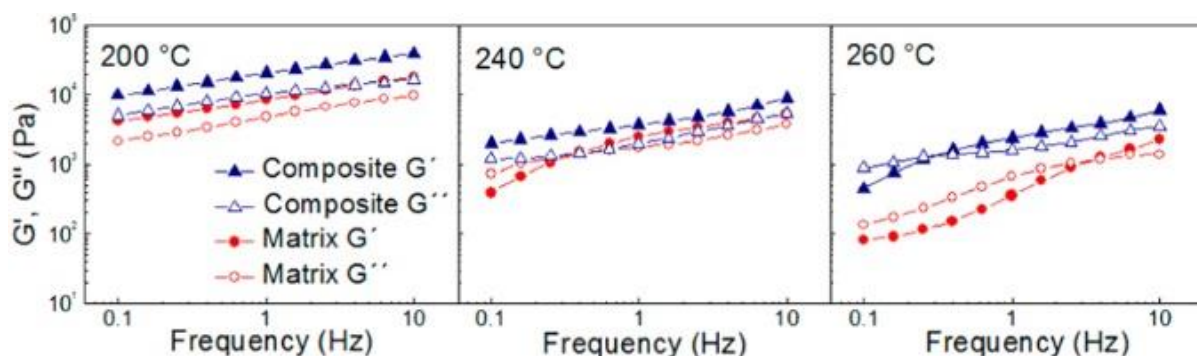


Figure 8. Frequency dependence of storage (G') and loss modulus (G'') [79].

1.5.4 Thermal conductivity

Some sorts of electrically conductive fillers may be combined with polymer matrixes to design conductive composites. In order to evaluate thermal activity performance, many investigators have used several methods to determine the thermal conductivity [71]. Generally, the mechanical energy output of shape-memory actuators is determined by the relationship between recoverable stress and strain (shape deformation) [80]. Thus, mechanical properties (Young's modulus) and the capability for heat transfer absorbed by light are important for light-induced stress recovery. The reinforcement and enhanced thermal conductivity of nanocomposites are shown in Figure 9. Through the well-dispersed filler in the composite, one can observe synergic effect in shape-change enhanced by thermal conductivity.

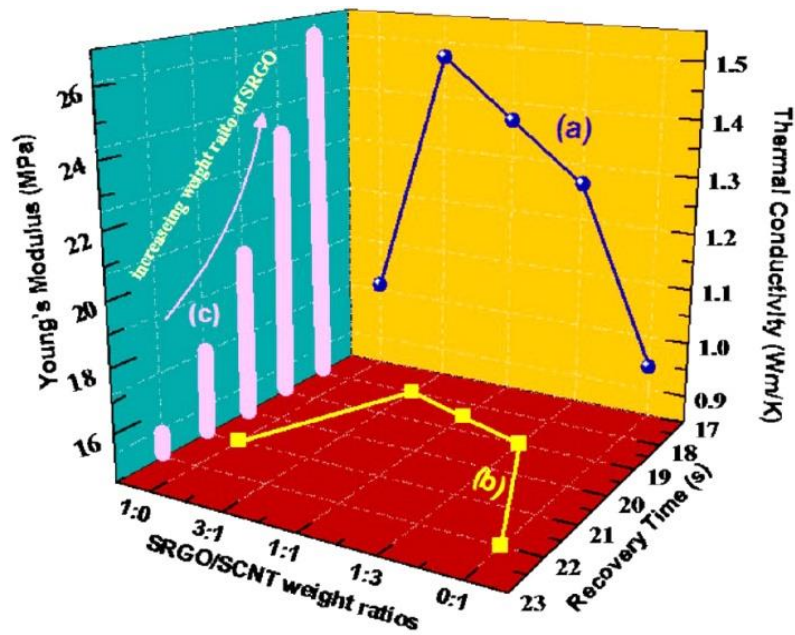


Figure 9. Thermal conductivity (a), the recovery time (b), and Young's modulus of composites (c). [80].

1.6 Methods for determination of photo-actuation behavior

Due to unusual composition of photo-actuating systems a numerous different approaches were settled to investigate photo-actuating ability. The properties of these systems are typically evaluated in absence or presence of the stimulus, usually light in off or on state.

1.6.1 Dynamometer

One of the setups used to measure PA behavior is the use of dynamometer [56, 81] as is shown in Figure 10. Sample in the strip-shape is fixed into two clamps horizontally, on the both sides of the strip. On the bottom clamp, the weight of several values is attached. Therefore, the preliminary strain is applied. The strip is exposed to the light (ordinarily LED light or laser beam) and then the change in the horizontal dimension is measured. However, the method is fast and the setup is easy to build, materials with different mechanical properties, reported different pre-strain with the same pre-load applied. Thus, the adjusting to certain pre-strain is rather impossible using various weights [33].

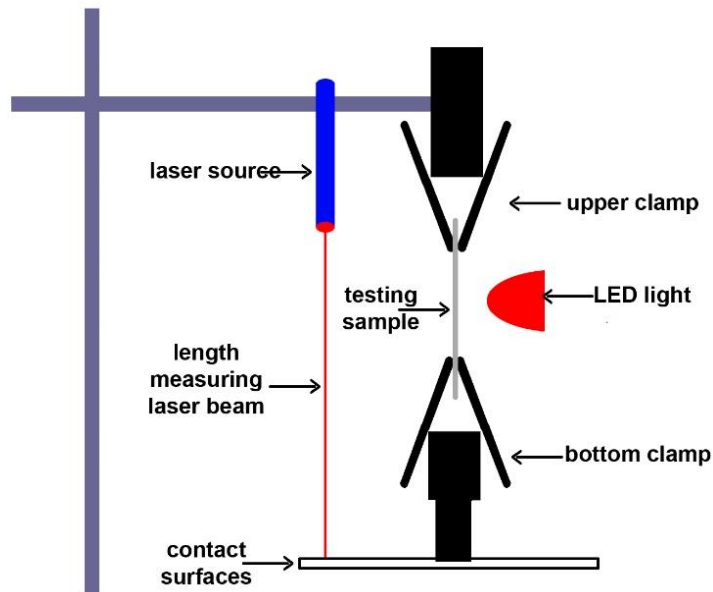


Figure 10. Dynamometer setup used for determination of photo-actuation behavior [33].

1.6.2 Thermomechanical analysis

More accurate method using same principle is, measuring sample with thermomechanical analyzer. Compared to the previous setup, this device is very accurate and a certain value of pre-strain can be finely tuned. The TMA device is able to collect the data each 0.1 s depending on the settings and is able to record the change in the length automatically with very high precision usually in 0.1 μm scale [33, 78, 79, 82].

1.6.3 Dynamic mechanical analysis

The one of the best solution to measure photo-actuation is dynamic mechanical analysis in iso-strain tensile mode (Figure 11). The sample is stretched between two clamps and pre-strain is set. The sample stress is stabilized and then the light is applied. Due to the precise sensor, which calculates the position of the clamps, the device record very accurately the load stress caused by actuation of light-stimulated sample. However, DMA is very accurate, some samples cannot be investigate by this method, because, they are not possible to possess such load stress that can be record by the device [56].

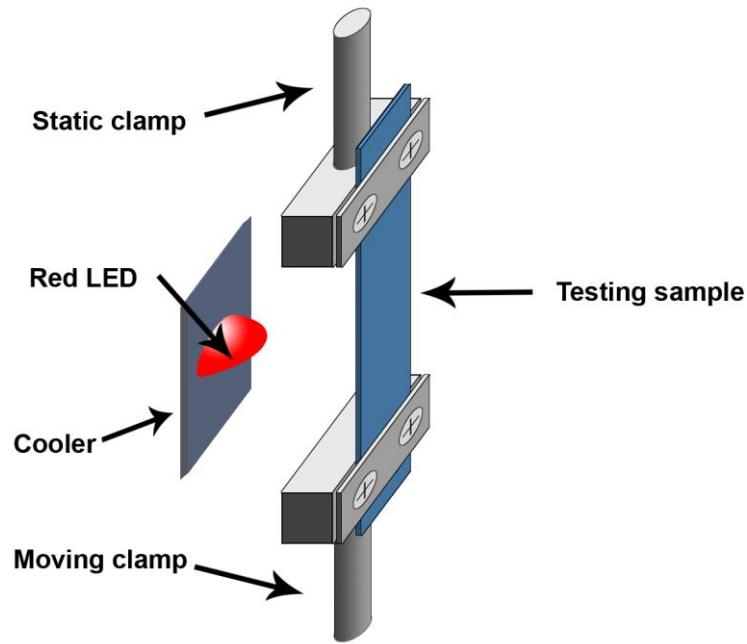


Figure 11. DMA setup for photo-actuation investigation [56].

1.6.4 Atomic force microscopy

Several photo-actuation performance measurements were done by Atomic force microscopy (AFM). This device detects material shape-change through the AFM tip that is placed on the top of the material, as can be seen in the Figure 12. After exposition of sample to the light, the AFM record the tip movement. Although, this technique is suitable to investigate the PA kinetics, there is no option how to calculate the actuation stress and the measurement of the displacement is limited due to the limitation of the AFM tip movement.

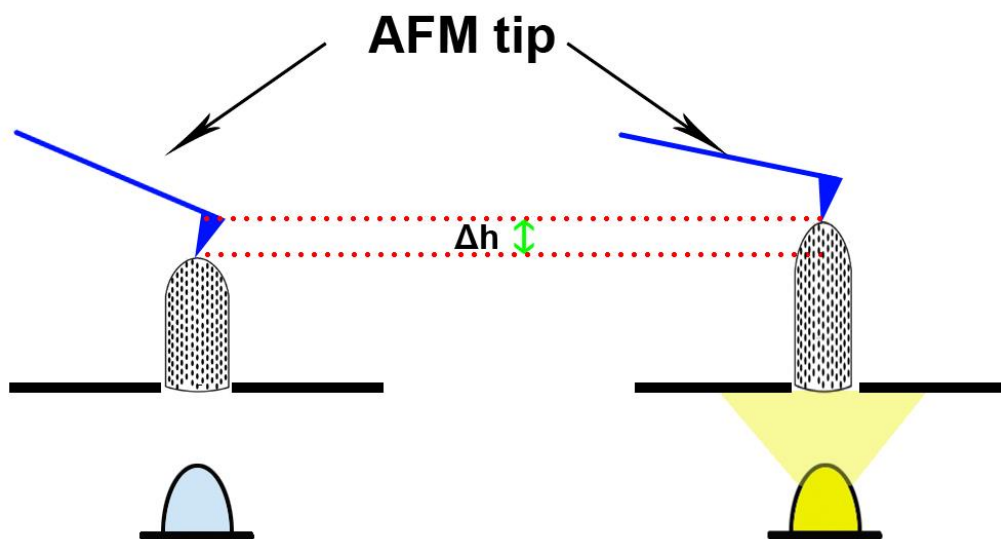


Figure 12. AFM device for determination of the photo-actuation performance [57].

1.7 Drawbacks of the current systems

Despite the enhanced properties, the composites suffer from several drawbacks, which hinder their potential. One of the issue is the poor compatibility of the filler in the matrix. The key role in performance of PA system plays the interface between the particles and the matrix. The elastomeric matrix is usually hydrophobic and particles are hydrophilic or of very different nature with considerably foreign surface properties, from the surface energy point of view. Due to this issue, particles usually form aggregates and their distribution in the system is very poor, and thus lead to the decreased thermal conductivity and unsuitable mechanical properties of the final composite structure.

Another problem is the tenuous deformation of the composite, resulting from weak interaction between filler and matrix, which leads to reducing of the mechanical properties and finally the PA capability and repeatability of the phenomenon.

1.8 State of the art

In order to reduce drawbacks of the PA systems, several techniques and procedures have been investigated. As specified in the beginning, this work was dedicated to photo-actuating systems along with the performance enhancements of the structures through particle's modifications. Indisputably, a big amount of PA research has been done in field that deals with just photo-switchable polymeric films or composites consists of elastomeric matrix and filler which is usually pure carbon-based nanoparticles or nanotubes [73].

Many investigations deal with different photo-actuated materials resulting to different reversible shape-change performances. General investigations are summarized in Table 1.

Table 1. Typical components, benchmark performance, and features of these schemes [73].

Typical components	Benchmark performance	Strengths and weaknesses
- CNT/polymer composites	- High-loading capacity: up to 140 times its own weight	- High energy conversion efficiency
- Gradient rGO/GO structure	- Fast response time and displacement rate: up to 0.3 s at 14 cm/s	- Wide light source wavelength range
- Graphene/polymer composites	- Large deformation: up to 479° for bending, 30–400% for contraction, 36° s ⁻¹ for rotation - Cycling durability: 60000 cycles at ≈2 Hz	- Fast response
- Graphite/polymer		- Multiple deformation modes
- Amorphous carbon/polymer composite		- Reversible deformation
		- Certain ambient conditions (temperature, humidity, air pressure, etc.) required
		- Large CTE mismatch required

In one of the studies [83], authors fabricated visible-light-responsive actuators with diverse and tunable deformations by embedding aligned CNTs in paraffin wax on a polyimide substrate. The aligned CNTs play role as cellulose fibrils, and the paraffin wax look like the soft cells/tissues of a plant. Depending on alignment

of the CNTs, the prepared strips performed different actuation. The samples expanded perpendicularly in orientation of aligned CNTs. the edges of the CNT/paraffin wax composite film extended outward by 28 μm along the transverse direction.

Another work, [84], deals with modified of graphene-based filler. Surface of graphene was modified by polydopamine and grafted by poly(N-isopropylacrylamide (PNIPAM)). The polymer brushes PNIPAM possess flower-form structures, which change their shape after light stimulation. The authors prepared monolayers of this material and encapsulated them into live cells.

In a different investigation [85] light-driven bilayer composite comprising an IR-sensitive reduced graphene oxide in PDMS polymeric composite as an active layer and an IR-inert PDMS as a passive layer, was developed. These bilayer sheets with excellent responsive bending properties and high mechanical properties were used as active hinges for remote construction of complex 3D configurations (such as bidirectionally folded columns, boxes, pyramids, and cars) that demonstrated the three capabilities of these bilayer composites. Their large deformation and excellent stability, their ability to produce complex structures, and their remote-autonomous assembly upon IR irradiation.

In this work [86] authors constructed the rolled CNT/polymer bilayer composite actuators. This actuator with tubular shape exhibits electrically and sunlight-induced actuation with fast response, large deformation, and multiform biomimetic motions through simple configuration design. After light exposure, sample shows mechanical actuation, from flat shape to roller shape, the angle change was 280° in 0.83 s.

Further study [87] demonstrated a novel method of mixing graphene oxide with polycarbonate membrane to form a bilayer assembly through vacuum filtration technique. When IR light stimulated the GO face of GO/PC bilayer, the bilayer foil started deflecting from its equilibrium position rapidly with a response time of less than 1 s. The deformation then grew with time and reached its maximum value i.e. 12 mm within 3 s.

1.9 Synthesis of core-brush nanoparticles

However, GO particles are could serve as very good filler in composites due to their relatively easy preparation process, large surface area, possibility to enhance overall performance of various matrices, they are quite inert, which conclude to poor dispersibility, weak filler/matrix interaction which leads to the local inhomogenities and finally to bad heat distribution through the system. To solve this problem, particles have to be modified. One of the solution is the grafting of polymer brushes onto the surface of the particles. Polymer brushes create a layer on the surface of particles, which prevents their aggregation, enhance their compatibility to the matrix etc. The most common approaches for covalent attachment of macromolecular chains on to GO surface can be classified as “grafting-to”, “grafting-from” and “grafting through” [88].

1.9.1 Grafting-to approach

In this technique, the polymer is firstly synthesized and then covalently link to the surface of the particle, which possess with a reactive group. This approach shows the benefit of being relatively simple, although the number of functional groups per surface area (grafting density) that can be obtained is both kinetically and thermodynamically limited [89]. Once, the surface is covered by polymer brushes, the polymer concentration at interfaces becomes larger than in solution. This leads to slowing down the immobilization reaction at the surface and decreasing of attachment rate. Another problem is that this approach creates impurities of non-grafted chains [90].

1.9.2 Grafting-from approach

On the other hand, grafting-from strategy is based on the growth of polymer brushes from the surface by using initiator, which is attached to the particle [91]. This method is also known as surface-initiated polymerization and is typically used for synthesis of inorganic-organic core-brush morphologies [88]. It has been assumed as an effective technique to control the interfacial behavior [92]. First, the initiator is immobilized at the surface and then the polymer chain start to growth from this initiator species. Contrary previous method high grafting density can be obtained [93].

1.9.2.1 Free radical polymerization

This method of polymerization is the most commonly used for synthesis of commercially available polymers. This is caused by many attractive characteristics that this method possesses. It is applicable to the wide range of monomers and copolymers with any functional group, compared to other polymerization methods it has higher tolerance to the water and other impurities, a wide range of temperatures, available media can be used as suitable reaction conditions, and it is cheaper compared to other technologies [94]. Although many advantages mentioned above, free radical polymerization is an uncontrolled process, which has no capability of controlling polymer architecture, i.e. molecular weight and molecular weight distribution of the grafts. The reaction begins with the generation of free radical spots on the main backbone that react with the vinyl or acrylic monomer to propagate a new polymer chain covalently bonded to the backbone. Finally, grafted chains terminate through termination or chain transfer reactions [92].

1.9.2.2 Nitroxide-Mediated Polymerization (NMP)

This polymerization method belongs to the group of the stable free radical polymerization procedures. It is built on the usage of a stable nitroxide radical. It appears to be very simple technique because it needs only addition of a proper alkoxyamine to the polymerization medium. The propagating species reacts with a stable radical to form dormant species. The resulting dormant species can then reversibly cleave to transform the free radicals [92]. The chain is starting to grow

until the monomer is consumed. This method is usually used for styrene and acrylate monomers [95].

1.9.2.3 Atom transfer radical polymerization (ATRP)

ATRP is great technique for grafting polymer brushes, which allows precisely control the chemistry of size, functionalities and construction of the polymers as well as to achieve the identical growth of all the chains [96]. The mechanism of ATRP is depict by Figure 13.

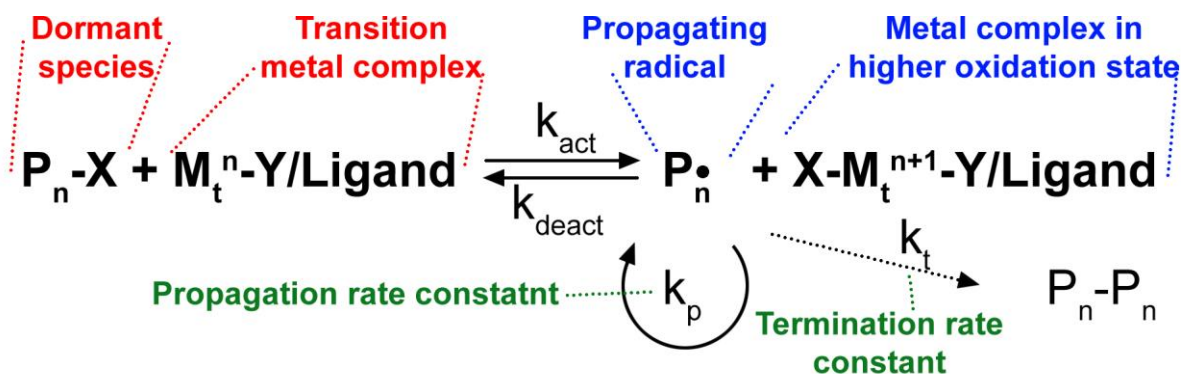


Figure 13. Scheme of the ATRP reaction [97].

ATRP is based on an inner sphere electron transfer procedure, which contains a reversible halogen transfer from a dormant species to a transition metal complex [97]. This leads to formation of propagating radicals and the metal complex in higher oxidation state. Polymer chains grow by the connecting monomers to the created radicals. They respond reversibly with the oxidized metal complexes, a dormant species and the transition metal complex in the lower oxidation state. Radicals also terminate with the rate constant of termination [98]. ATRP can be used on the nearly all of vinyl and acrylic monomers over wide temperature range. ATRP controls the sustained radical effect; therefore, the concentration of catalyst should be high to maintain a high polymerization rate [99]. In these high concentrations, most of metal catalysts are expensive and toxic, thus to remove them from the polymer needs expensive and time-consuming techniques [92].

1.9.3 Grafting-through

This strategy is also known as the macromonomer method and it could be reputed as in-between method of previously described techniques. The polymerizable groups are anchored onto the surface of nanoparticles. The reaction solution contains initiator, monomers and modified nanoparticles, which play role as crosslinking agent. Thus, both monomers copolymerize and the inorganic phase is incorporated inside polymer chains [100]. This process is not much explored from scientific point of view and the mechanisms that control the polymerization progression are not entirely understood [101].

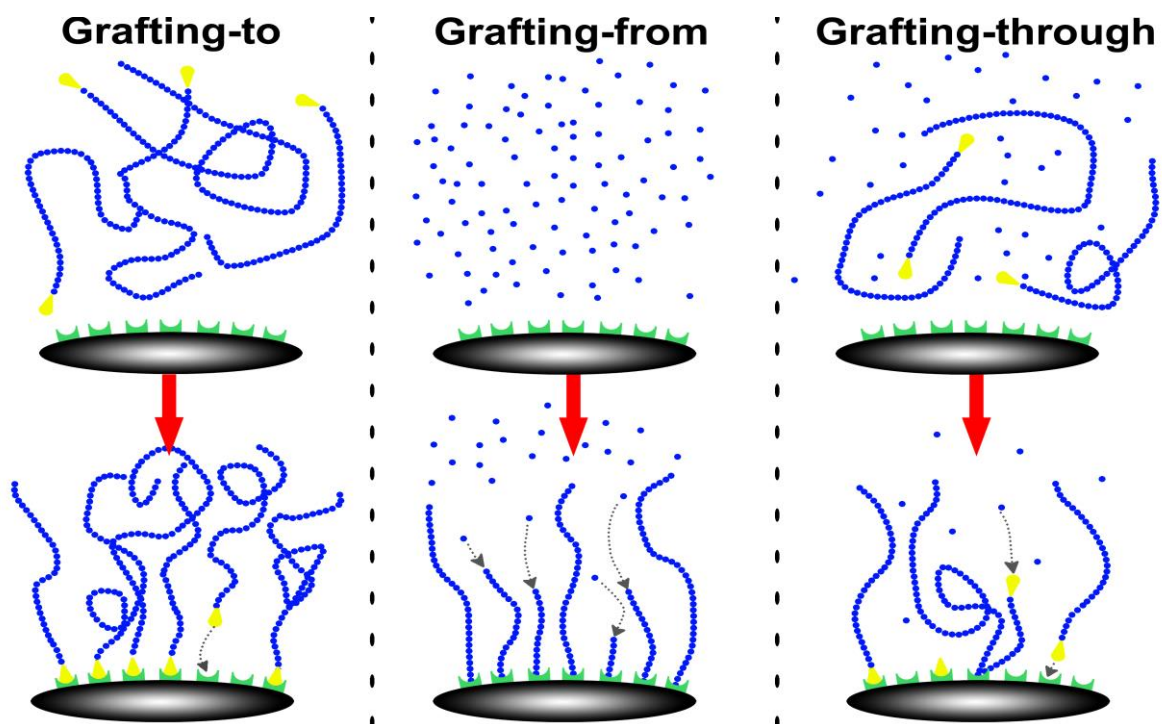


Figure 14. Schematic presentation of grafting-to, grafting-from and grafting-through techniques. Blue dots representing monomer, blue chain represents polymer, yellow shape is functional group, green shape is surface-attached initiator [92].

2 MOTIVATION AND AIMS OF THE DOCTORAL STUDY

2.1 Motivation

The PA systems belong among intelligent materials that can reversibly change their physical properties after the application of external light. These materials play a significant role in many industries ranging from civil to biomechanical engineering.

2.2 Aims of the doctoral study

The main aim of this thesis was to analyze and compare the performance properties of the PA systems containing differently ATRP-grafted graphene oxide particles. The key tasks were defined as follows:

- a) Complex study of physical and chemical aspects affecting the performance of the PA systems,
- b) Synthesis and preparation of novel particles with tailored properties via SI-ATRP, which could be successfully used as active fillers in PA systems in order to improve their PA performance,
- c) Analysis of the modified particles and their influence on mechanical properties, compatibility with polymer matrix and thermal conductivity of the systems.
- d) Analysis of the effect of the particles modification on the PA performance and physical properties. Evaluation of the system's efficiency by comparing their properties with unmodified GO particles.

3 SUMMARY OF RESULTS

This thesis deals with the synthesis of particles and their modification via surface-initiated ATRP and their possible use in the PA systems in order to reduce the outlined drawbacks. Due the fact that most of the papers are connected via SI-ATRP technique, synthesis and general characterization of the particles are firstly specified. Additional, the most significant results of the individual papers are stated.

3.1 Preparation of graphene oxide particles

In order to find good conductive material, it was decided to prepare our own graphene oxide particles, with capability of easy and accurate way of changing their conductivity. There are several methods to prepare GO particles from graphite [102-104].

GO was prepared according to modified Hummer's method [105]. GO was fabricated from graphite powder. The raw graphite was stirred with concentrated sulfuric acid. Subsequently, sodium nitrate and potassium permanganate were gradually added. The mixture was additionally stirred then the deionized water was added. Finally, concentrated hydrogen peroxide was added, and the solution turned its color into brilliant brown, which indicated complete oxidization of graphite. The product was separated in a high-speed centrifuge. The cleaning routine was based on dispersion of the GO in hydrochloric acid, and the re-separation in a centrifugal field. The particles were lyophilized in order to remove the residual water after the purification process.

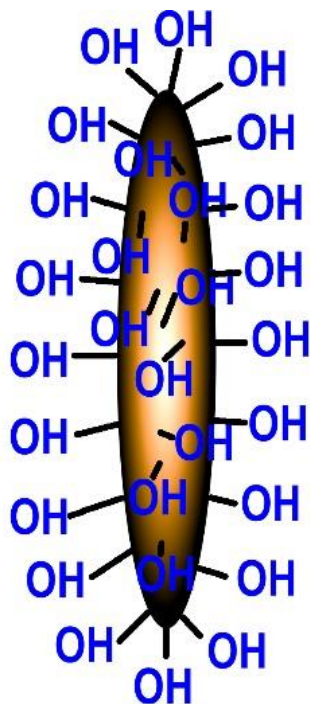


Figure 15. Functional groups of Hummer's method [1].

3.2 Modification of GO particles through SI-ATRP

The problem with GO particles is with their bad affinity to matrixes and attribute to coagulate and sediment. To enhance particles attraction to matrix and reduce their sedimentation and coagulation process, GO particles were grafted with polymer via SI-ATRP [106]. The GO particles were modified via amidation reaction with α -Bromoisobutyryl bromide (BiBB). The particles were then washed and dried. Finally, the initiator-modified GO sheets were grafted with poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA), poly(glycidyl methacrylate) (PGMA) or poly(trimethylsilyloxyethyl methacrylate) (PHEMATMS) under precise argon atmosphere. Through different ratio between monomer, initiator, ligand (N,N,N',N'',N''-Pentamethyldiethylenetriamine) (PMDTA) and catalyst (CuBr) by length of reaction mixing and changing them reaction temperature, the length of resulting polymer chains is easy to control.

The GO particles modified by PMMA and PMMA were utilize to prepare photo-actuators in order to investigate polymer compatibility to the chemically (PDMS) and physically Poly(propylene-co-ethylene) cross-linked matrix (Paper I, IV). Particles grafted with PGMA in different molar ratio of reactants were prepared to investigate compatibility to the matrix (PDMS) and graphene oxide reduction (Paper II). The PHEMATMS is hydrophobic, hence we expected the silyl-based polymer would improve the interaction of GO particles with PDMS served as matrix (Paper III).

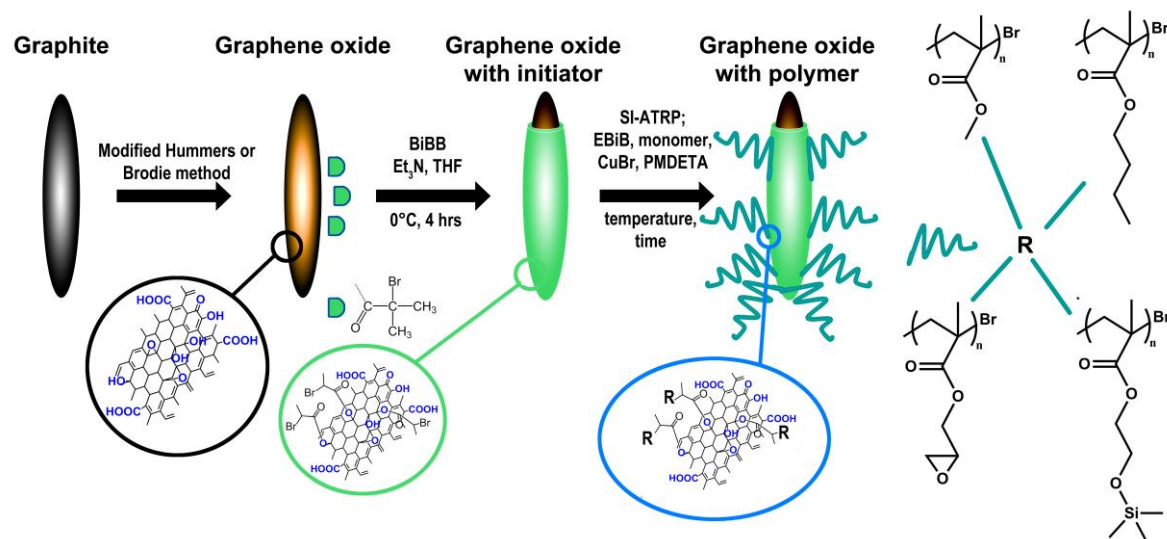


Figure 16. Immobilization of BIBB initiator on functionalized GO particles with their subsequent grafting with polymer via SI-ATRP [105].

For each reaction, the molar ratio between the monomer and the initiator was defined in order to obtain the desired polymer chain length, which was theoretically designated before the experiment. The determination of the molecular weight was able due to the presence of a free initiator ethyl α -bromoisobutyrate (EBiB) in reaction. The molecular weight was investigated by

gel permeation chromatography (GPC) and monomer conversion was calculated using nuclear magnetic resonance (NMR). The results were evaluated according to the literature [107] and are summarized in Table 2.

Table 2. Molecular characteristics of prepared GO particles

Sample name	Mono mer	Initia tor	Liga nd	Catal yst	M_n ($\text{g}\cdot\text{mol}^{-1}$)	DP_n (-)	PDI (-)	Convers ion (%)
GO-PMMA	100	1	4	1	5600	56	1.18	89
GO-PBMA	100	1	4	1	5200	37	1.21	91
GO-PGMA 1	100	1	2	1	5900	42	1.28	43
GO-PGMA 2	100	1	4	1	6100	43	1.26	46
GO-PHEMATMS	100	1	4	1	12600	62	1.19	67
GO-PMMA-V	100	1	4	1	6800	68	1.18	89
GO-PBMA-V	100	1	4	1	5800	41	1.21	89

3.3 Characterization of prepared grafted and non-grafted GO particles

Results, which describe grafted and non-grafted GO particles characteristics obtained from each paper (P), are summarized in Table 3. Raman spectroscopy served to show variation in I_D/I_G ratio which indicates the reduction of GO which also leads to higher electrical conductivity (Cond.). This enhance the heat distribution through the composite system. Contact angle measurement (CA) was performed to prove GO particles affinity to the matrix. Small droplet of siloxane was added to the GO pellet and in all cases, modified GO particles posses with lower CA, which means that they are more compatible to the matrix, thus the better dispersion could be reached.

Table 3. Results from measurements done on GO particles

Paper	Material	I_D/I_G (-)	CA ($^\circ$)	Cond. ($\text{S}\cdot\text{cm}^{-1}$)	Other measurements done
P I	Neat GO	0,90	49.9	2.1×10^{-7}	$^1\text{H NMR}$, TEM, TGA-FTIR, GPC, AFM
	GO-PMMA	1.05	38.7	6.3×10^{-8}	
	GO-PBMA	1.08	28.7	2.1×10^{-7}	
P II	GO-PGMA1	1.08	40.1	5×10^{-7}	$^1\text{H NMR}$, TEM, TGA-FTIR, GPC
	GO-PGMA2	1.26	40.1	2.3×10^{-3}	
PIII	GO-PHEMATMS	1.09	26.3	6×10^{-7}	$^1\text{H NMR}$, TEM, TGA-FTIR, GPC
P IV	GO-PMMA	1.05	-	6.3×10^{-8}	$^1\text{H NMR}$, GPC, TGA-FTIR, TEM, XPS
	GO-PBMA	1.08	-	2.1×10^{-7}	

3.4 Characterization of composites

The composites properties are depicted in Table 4. For each composite the dielectric spectroscopy was measured. The flexibility of the polymer matrix is given by two factors, mobility of the main chain characterized by α relaxation, corresponding to T_g , and side chains mobility characterized by α' relaxation, indicating how the entanglements of side chains are stiff. Therefore, both relaxation were investigated using Arrhenius equation. The activation energy (E_a) of α relaxation is significantly shifted to the lower values after grafting the particles, indicating the improved flexibility of the polymer matrix. Thermal conductivity (TC) shows the slightly increase which is resulting to the better heat distribution through the composite.

Table 4. Composite performance with grafted and non-grafted GO particles in 0.1 vol. % concentration

Paper	Material	E_a (kJ·mol ⁻¹)	TC (W·mK ⁻¹)	Δl (μ m)	ε (%)	Other measurements
P I	neat PDMS	45.70	0,071	7,1	0,071	DMA, Diel. spectroscopy
	GO/PDMS	36.57	0.144	9.1	0.091	
	GO-PMMA/PDMS	35.99	0.153	9.4	0.094	
	GO-PBMA/PDMS	25.39	0.151	11.8	0.118	
P II	GO-PGMA 1/PDMS	31.32	0.152	12.50	0.125	DMA, Diel. spectroscopy
	GO-PGMA 2/PDMS	23.80	0.161	20.20	0.202	
P III	GO-PHEMA/PDMS	22.01	-	34	0.34	DMA, Diel. spectroscopy
P IV	neat Vistamaxx	-	0.89	12	0.12	Rheology
	GO/Vistamaxx	-	0.156	20	0.2	
	GO-PMMA/Vistamaxx	-	0.196	30	0.3	
	GO-PBMA/Vistamaxx	-	0.202	68	0.68	

The photo-actuation performance was studied for various composite structures, and the influence of the filler modification and the filler loading on the final properties was explained. Substantial part of the work deals with photo-actuation of composites in which filler is modified GO by different polymer brushes, and matrix is cross-linked PDMS (Paper I, II, III). Paper IV discuss the PA performance of PMMA and PBMA modified GO particles in thermoplastic elastomer matrix, specifically, poly(ethylene-co-propylene) (Vistamaxx). The dimension change in absolute value are explained by Δl . To compare PA performance with other scientific researches the relative value of prolongation was counted (ε)

$$\varepsilon = \frac{\Delta l}{l_0} \times 100 \quad (7)$$

where Δl is the dimension change in absolute value and l_0 is the initial length of the sample.

The Figure 17 shows difference in PA deformation for four different samples. Neat PDMS matrix maximum value of actuation was ΔL , was $7.1 \mu\text{m}$. With addition of 0.1% of GO particles, this value increased to $9.1 \mu\text{m}$, which was caused by improved heat transfer. The matrix with modified GO particles performed even higher ΔL value, $9.4 \mu\text{m}$ and $11.8 \mu\text{m}$ for GO-PMMA and GO-PBMA respectively. The reason for this behavior is due to proper incorporation of the particles into PDMS matrix, which causes better shape recovery and improved heat transitions within the samples.

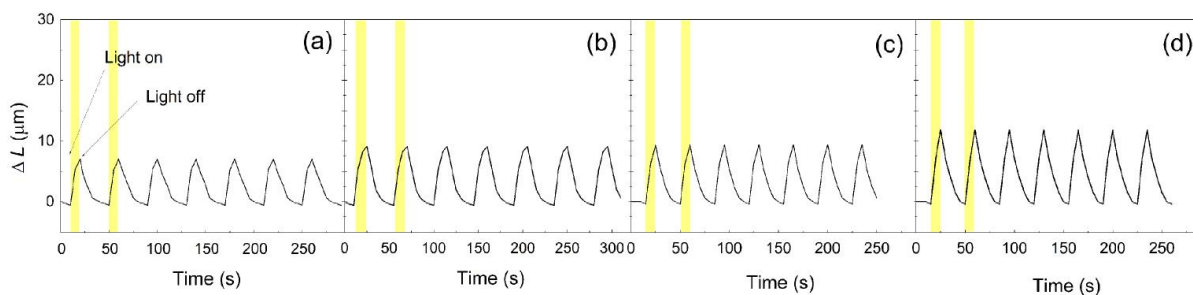


Figure 17. Photo-actuation performance of the pure PDMS (a) and the PDMS composites containing 0.1 vol % of neat GO (b), GO-PMMA (c) and GO-PBMA (d) [108].

By using TPE matrix, the PA performance is even better compared to PDMS matrix. Composites containing the same filler but vistamaxx matrix show significant enhancement in shape change in dimension as it can be seen in Figure 18.

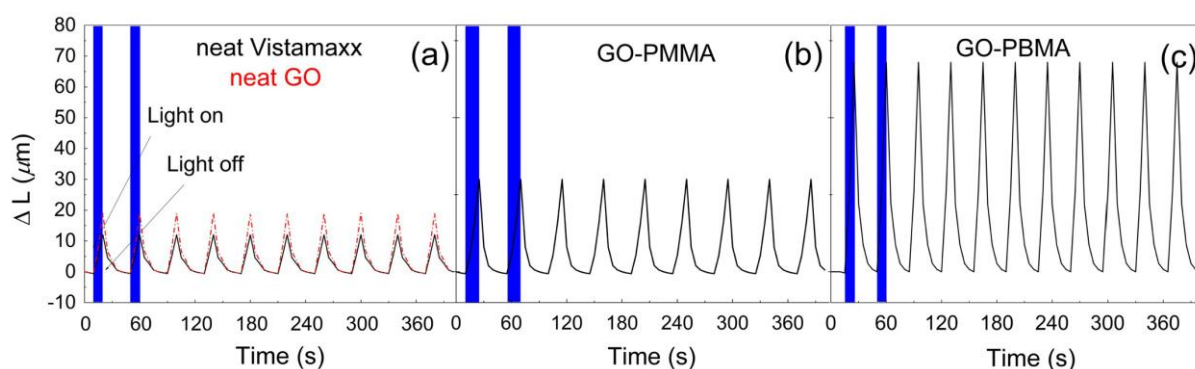


Figure 18. Photo-actuation performance of neat vistamaxx and composite containing 0.1 vol.% of neat GO (a), GO-PMMA (b) and GO-PBMA (c) [20].

After increasing of GO particles concentration in the system to the 1 vol.% the maximum actuation value was roughly five times higher as it is showed in Figure 19. The main reason for this significant enhancement was already proposed by earlier researches and is likely the improved flexibility of the polymer composite, which was confirmed by the lower activation energy, higher damping and

enhanced thermal conductivity, improving the heat delivery within the composite samples [108].

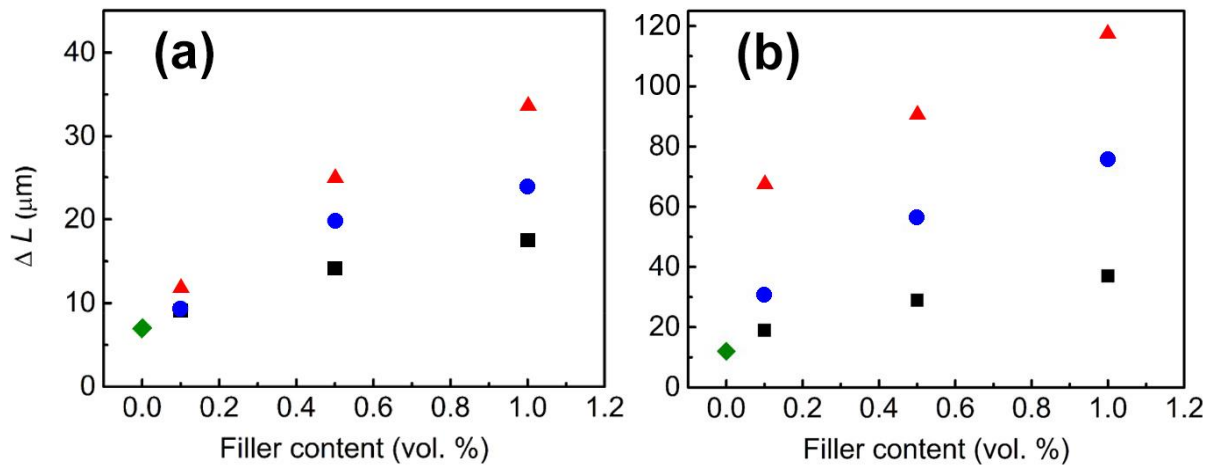


Figure 19. Dependence of the filler content on the change in the length for the pure matrix (green diamond), GO-PMMA (black squares), GO-PBMA (red triangles) for composite with PDMS (a) and Vistamaxx (b) matrix [20, 108].

4 CONTRIBUTIONS TO THE SCIENCE

The main outputs and crucial points of this doctoral study those are beneficial to the both, scientific audience as well as industry, are highlighted below:

- SI-ATRP modification of GO particles with various monomeric systems.
- Confirmation that the simultaneous reduction of GO and modification with polymer brushes is possible for variety of monomers.
- Developed PA device based on thermo-mechanical analyzer which was applied as national utility model no. 31633, named " Zařízení pro sledování změny rozměrů vlivem světelné stimulace".
- Improved compatibility between the polymer matrix and GO particles due to the SI-ATRP modification and knowledge how the similarity of the grafting moiety contribute to this compatibility.
- Improved and homogenous dispersibility of the GO-grafted filler in polymer matrix which contribute to enhanced thermal conductivity.
- Direct comparison of PA performance between the chemically cross-linked systems and TPEs.
- Showed that various filler content and various light intensities can alter the final PA capability.
- Confirmation, that SI-ATRP approach used of GO modification can be effectively applied for filler modification and subsequently mixed into the elastomeric matrix, those capabilities are in the range suitable to be applied as pre-stretched films in the tactile display systems.

CONCLUSIONS

Some of the common drawbacks of conventional PA systems were successfully eliminated using novel approach based on the fabrication of the precisely grafted GO particles via SI-ATRP. The modification of particles were done in controlled regime; hence, the possible of prepared materials exceeded the properties of the systems without modification.

In conclusion, this thesis summarizes utilization of GO particles modified by different polymer chains and also using different matrix that significantly improved the PA ability of whole systems. Due to this modifications, the GO particles possessed better compatibility to matrices, such as chemically cross-linked PDMS or thermoplastic elastomers based on polyolefins and led to enhanced dispersion through the matrix, therefore the heat distribution could be easily transferred into the entire composite. The PA ability was verified by system based on thermo-mechanical analysis, which confirmed the significantly enhanced photo-actuation capability (in some cases even more than ten times higher) compared to neat matrix material and in contrast to other publications as well as systems containing unmodified particles.

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LIST OF SYMBOLS AND ABBREVIATIONS

^1H NMR	Proton nuclear magnetic resonance
AFM	Atomic force microscopy
BiBB	α -Bromoisobutyryl bromide
CA	Contact angle
CNT	Carbon nanotubes
DMA	Dynamic mechanical analysis
DP_n	Degree of polymerization
E'	Storage modulus
E''	Loss modulus
E_a	Activation energy
EBiB	Ethyl α -bromoisobutyrate
EVA	Poly(ethylene-co-vinyl acetate)
FTIR	Fourier-transform infrared spectroscopy
GO	Graphene oxide
GPC	Gel permeation chromatography
IR	Infrared light
k	Boltzmann constant
LB	Langmuir-Blodgett films
LCPs	Liquid-crystalline polymers
LED	Light-emitting diode
M'	Storage dielectric modulus
M''	Loss dielectric modulus
M^*	Complex dielectric modulus
M_n	Molecular weight
PA	Photo-actuation
PBMA	Polybutylmethacrylate
PDI	Polydispersity index
PDMS	Poly(dimethyl siloxane)
PGMA	N,N,N',N'',N'''-Pentamethyldiethylenetriamine
PHEMATMS	Poly(trimethylsilyloxyethyl methacrylate)
PLZT	Lead zirconate titanate
PMDTA	N,N,N',N'',N'''-Pentamethyldiethylenetriamine
PMMA	Polymethylmethacrylate
PNIPAM	poly(N-isopropylacrylamide)
POA	Photo-induced Optical Anisotropy
R	Universal gas constant

SI-ATRP	Surface-initiated atom transfer radical polymerization
SIS	Polystyrene-block-polyisoprene-block-polystyrene
T	Temperature
TC	Thermal conductivity
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
TPE	Thermoplastic elastomer
UV	Ultraviolet
VIS	Visible
XPS	X-ray photoelectron spectroscopy
ϵ	Relative shortening
ϵ^*	Complex permittivity
ϵ'	Relative permittivity
ϵ''	Loss permittivity
τ	Relaxation time
τ_0	Pre-exponential factor

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Training Abroad	
Dates	09/2020 – 11/2020 Student traineeship at Lodz University of Technology, Institute of Polymers and Dye Technology (Poland)
Field of Study	Modification of surfaces by branched polymer chains using SI-ATRP technique
Dates	12/2018 (1 week) Research period at Slovak Academy of Sciences, Polymer Institute (Slovakia)
Field of Study	Modification of graphene oxide particles via Atom Transfer Radical Polymerization
Expertise	
Fields	Polymer processing, Mechanical properties of polymers, Polymer synthesis
Other Languages	
	Level
English	C1
German	A1
Awards	
	Best Poster Award (co-author) – 2017, Miskolc (Hungary), Conference paper “ <i>Ferrous oxalate micro-rods as a promising material for electrorheology</i> ”

LIST OF PUBLICATIONS

Publications in the Journals with Impact Factor:

- [1] ZYGO, M.; MRLIK, M.; ILCIKOVA, M.; HRABALIKOVA, M.; OSICKA, J.; CVEK, M.; SEDLACIK, M.; HANULIKOVA, B.; MUNSTER, L.; SKODA, D.; URBANEK, P.; PIETRASIK, J.; MOSNACEK, J. Effect of Structure of Polymers Grafted from Graphene Oxide on the Compatibility of Particles with a Silicone-Based Environment and the Stimuli-Responsive Capabilities of Their Composites. *Nanomaterials*. **2020**, vol. 10, no. 3, pp.
- [2] OSICKA, J.; MRLIK, M.; ILCIKOVA, M.; KRUPA, I.; SOBOLCIAK, P.; PLACHY, T.; MOSNACEK, J. Controllably coated graphene oxide particles with enhanced compatibility with poly(ethylene-co-propylene) thermoplastic elastomer for excellent photo-mechanical actuation capability. *Reactive & Functional Polymers*. **2020**, vol. 148, no., pp.
- [3] SEDLACIK, M.; OSICKA, J.; PAVLINEK, V.; FOJTL, L. The influence of ultraviolet radiation on the optical properties of glass fibre reinforcements for polyurethane matrix composites. *Coloration Technology*. **2019**, vol. 135, no. 6, pp. 510-15.
- [4] MRLIK, M.; ILCIKOVA, M.; OSICKA, J.; KUTALKOVA, E.; MINARIK, A.; VESEL, A.; MOSNACEK, J. Electrorheology of SI-ATRP-modified graphene oxide particles with poly(butyl methacrylate): effect of reduction and compatibility with silicone oil. *Rsc Advances*. **2019**, vol. 9, no. 3, pp. 1187-98.

- [5] KUTALKOVA, E.; MRLIK, M.; ILCIKOVA, M.; OSICKA, J.; SEDLACIK, M.; MOSNACEK, J. Enhanced and Tunable Electrorheological Capability using Surface Initiated Atom Transfer Radical Polymerization Modification with Simultaneous Reduction of the Graphene Oxide by Silyl-Based Polymer Grafting. *Nanomaterials*. **2019**, vol. 9, no. 2, pp.
- [6] DANKO, M.; KRONEKOVA, Z.; MRLIK, M.; OSICKA, J.; BIN YOUSAF, A.; MIHALOVA, A.; TKAC, J.; KASAK, P. Sulfobetaines Meet Carboxybetaines: Modulation of Thermo- and Ion-Responsivity, Water Structure, Mechanical Properties, and Cell Adhesion. *Langmuir*. **2019**, vol. 35, no. 5, pp. 1391-403.
- [7] OSICKA, J.; MRLIK, M.; ILCIKOVA, M.; MUNSTER, L.; BAZANT, P.; SPITALSKY, Z.; MOSNACEK, J. Light-Induced Actuation of Poly(dimethylsiloxane) Filled with Graphene Oxide Grafted with Poly(2-(trimethylsilyloxy)ethyl Methacrylate). *Polymers*. **2018**, vol. 10, no. 10, pp.
- [8] OSICKA, J.; MRLIK, M.; ILCIKOVA, M.; HANULIKOVA, B.; URBANEK, P.; SEDLACIK, M.; MOSNACEK, J. Reversible Actuation Ability upon Light Stimulation of the Smart Systems with Controllably Grafted Graphene Oxide with Poly (Glycidyl Methacrylate) and PDMS Elastomer: Effect of Compatibility and Graphene Oxide Reduction on the Photo-Actuation Performance. *Polymers*. **2018**, vol. 10, no. 8, pp.
- [9] MRLIK, M.; CVEK, M.; OSICKA, J.; MOUCKA, R.; SEDLACIK, M.; PAVLINEK, V. Surface-initiated atom transfer radical polymerization from graphene oxide: A way towards fine tuning of electric conductivity and electro-responsive capabilities. *Materials Letters*. **2018**, vol. 211, no., pp. 138-41.
- [10] MOSNACEK, J.; POPELKA, A.; OSICKA, J.; FILIP, J.; ILCIKOVA, M.; KOLLAR, J.; YOUSAF, A. B.; BERTOK, T.; TKAC, J.; KASAK, P. Modulation of wettability, gradient and adhesion on self-assembled monolayer by counterion exchange and pH. *Journal of Colloid and Interface Science*. **2018**, vol. 512, no., pp. 511-21.
- [11] MOSNACEK, J.; OSICKA, J.; POPELKA, A.; ZAVAHIR, S.; BEN-HAMADOU, R.; KASAK, P. Photochemical grafting of polysulfobetaine onto polyethylene and polystyrene surfaces and investigation of long-term stability of the polysulfobetaine layer in seawater. *Polymers for Advanced Technologies*. **2018**, vol. 29, no. 7, pp. 1930-38.
- [12] KUTALKOVA, E.; PLACHY, T.; OSICKA, J.; CVEK, M.; MRLIK, M.; SEDLACIK, M. Electrorheological behavior of iron(ii) oxalate micro-rods. *Rsc Advances*. **2018**, vol. 8, no. 44, pp. 24773-79.
- [13] OSICKA, J.; ILCIKOVA, M.; MRLIK, M.; MINARIK, A.; PAVLINEK, V.; MOSNACEK, J. The Impact of Polymer Grafting from a Graphene Oxide Surface on Its Compatibility with a PDMS Matrix and the Light-Induced Actuation of the Composites. *Polymers*. **2017**, vol. 9, no. 7, pp.
- [14] FILIP, J.; POPELKA, A.; BERTOK, T.; HOLAZOVA, A.; OSICKA, J.; KOLLAR, J.; ILCIKOVA, M.; TKAC, J.; KASAK, P. pH-Switchable Interaction of a Carboxybetaine Ester-Based SAM with DNA and Gold Nanoparticles. *Langmuir*. **2017**, vol. 33, no. 27, pp. 6657-66.
- [15] OSICKA, J.; ILCIKOVA, M.; POPELKA, A.; FILIP, J.; BERTOK, T.; TKAC, J.; KASAK, P. Simple, Reversible, and Fast Modulation in Superwettability, Gradient, and Adsorption by Counterion Exchange on Self-Assembled Monolayer. *Langmuir*. **2016**, vol. 32, no. 22, pp. 5491-99.
- [16] OSICKA, J.; ILCIKOVA, M.; MRLIK, M.; AL-MAADEED, M.; SLOUF, M.; TKAC, J.; KASAK, P. Anisotropy in CNT composite fabricated by combining directional freezing and gamma irradiation of acrylic acid. *Materials & Design*. **2016**, vol. 97, no., pp. 300-06.

Original Full Papers in Conference Proceedings (Indexed on Web of Science):

- [1] OSICKA, J.; MRLIK, M.; ILCIKOVA, M.; MOSNACEK, J.; LTD, T. ELECTORRHEOLOGICAL PERFORMANCE OF GRAPHENE OXIDE PARTICLES GRAFTED WITH POLY(ALPHA-METHYLSTYRENE) USING SI-ATRP APPROACH. 9th International Conference on Nanomaterials - Research & Application; **2018**.
- [2] MRLIK, M.; OSICKA, J.; SEDLACIK, M.; MOSNACEK, J.; LTD, T. MODIFICATION OF THE CARBONYL IRON PARTICLES USING SI-ATRP APPROACH WITH POLY(2-(1H-PYRROLE-1-YL)ETHYL METHACRYLATE). 9th International Conference on Nanomaterials - Research & Application; **2018**.
- [3] OSICKA, J.; CVEK, M.; MRLIK, M.; ILCIKOVA, M.; PAVLINEK, V.; MOSNACEK, J. Light-Induced and Sensing Capabilities of SI-ATRP Modified Graphene Oxide Particles in Elastomeric Matrix. Active and Passive Smart Structures and Integrated Systems 2017; **2017**.
- [4] MRLIK, M.; OSICKA, J.; ILCIKOVA, M.; PAVLINEK, V.; MOSNACEK, J. Smart composites based on controllably grafted graphene oxide particles and elastomeric matrix with sensing capability. Active and Passive Smart Structures and Integrated Systems 2017; **2017**.

Conference Contribution:

- [1] OSICKA, J.; CVEK, M.; KUTALKOVA, E.; MOUCKA, R.; SEDLACIK, M. Magnetorheological elastomers as a lightweight, transparent piezoresistive sensor. In: *ERMR 2019 – International Conference on Electrorheological Fluids and Magnetorheological Suspensions*, (ed. Li, W.), **2019**, Wollongong, Australia.
- [2] OSICKA, J.; MRLIK, M.; MUNSTER, L.; ILCIKOVA, M.; MOSNACEK, J.; SPITALSKY, Z. Photoactuable performance of graphene oxide attached by Poly [2-(trimethylsilyloxy)ethyl methacrylate] using SI-ATRP method in elastometric matrix. In: *ERMR 2018 - International Conference on Electrorheological Fluids and Magnetorheological Suspensions*, (ed. Wereley, N. M.), **2018**, College Park, Maryland, USA.
- [3] MRLIK, M.; OSICKA, J.; ILCIKOVA, M.; J., K.; MOSNACEK, J. SI-ATRP modification of poly(2-isopropenyl oxazoline) from the graphene oxide and its electrorheological performance. In: *ERMR 2018 - International Conference on Electrorheological Fluids and Magnetorheological Suspensions*, (ed. Wereley, N. M.), **2018**, College Park, Maryland, USA.
- [4] OSICKA, J.; MRLIK, M.; ILCIKOVA, M.; MOSNACEK, J. Electrorheological performance of graphene oxide particles grafted with poly(alpha-methylstyrene) using SI-ATRP approach In: *NANOCON 2017 - 9th International Conference on Nanomaterials - Research and Application*, (ed., **2017**, Brno, Czech Republic: TANGER LTD.
- [5] OSICKA, J.; CVEK, M.; MRLIK, M.; ILCIKOVA, M.; PAVLINEK, V.; MOSNACEK, J. Light-induced and sensing capabilities of SI-ATRP modified graphene oxide particles in elastomeric matrix. In: *SPIE - Smart Structures and Materials & Nondestructive Evaluation*, (ed. Gyuhae, P.), **2017**, Portland, Oregon, USA.
- [6] MRLIK, M.; OSICKA, J.; SEDLACIK, M.; MOSNACEK, J. Modification of the carbonyl iron particles using si-atrp approach with poly(2-(1H-pyrrole-1-YL)ethyl methacrylate). In: *NANOCON 2017 - 9th International Conference on Nanomaterials - Research and Application*, (ed., **2017**, Brno, Czech Republic: TANGER LTD.
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- matrix with sensing capability. In: *SPIE - Smart Structures and Materials & Nondestructive Evaluation*, (ed. Park, G.), **2017**, Portland, Oregon, USA.
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- [9] OSICKA, J.; R., M.; KASAK, P. Nicotinamide based supergelator with self-healing and thixotropic properties. In: *ARF 2016 - Qatar Foundation Annual Research Forum*, (ed., **2016**, Doha, Qatar.
- [10] KASAK, P.; OSICKA, J.; MRLIK, M.; ILCIKOVA, M. Anisotropic composite prepared by directional freezing and gamma irradiation. In: *Materials Science and Engineering Symposium*, (ed., **2015**, Doha, Qatar.

Utility models:

- [1] MRLIK, M., OSICKA, J. Instrument for shape-change monitoring upon light stimulation, 2018-34578, 2018, Czech republic.

Work on projects:

Position	Period	Project
Member of research team	2019-2021	Czech Science Foundation (GACR), <i>Nanotechnologies in flow-through electrochemical sensors applied in environmental engineering</i> , GJ20-27735Y
Member of research team	2018-2020	Czech Science Foundation (GACR), <i>Manufacturing and analysis of flexible piezoelectric layers for smart engineering</i> , GA19-17457S
Member of research team	2020	Internal Grant Agency of TBU in Zlín, <i>Influence of Modifications Dispersion Particles on the Utility Properties of Magnetorheological Systems</i> , IGA/CPS/2020/006
Member of research team	2017-2019	Czech Science Foundation (GACR), <i>Novel Magnetorheological Elastomers Based on Modified Magnetic Fillers</i> , GA17-24730S
Principal investigator	2019	Internal Grant Agency of TBU in Zlín, <i>Influence of organic materials on the efficiency of intelligent systems</i> , IGA/CPS/2019/005
Principal investigator	2018	Internal Grant Agency of TBU in Zlín, <i>Preparation and characterization of electrorheological suspensions based on ferrous oxalates and clays</i> , IGA/CPS/2018/004
Member of research team	2016-2018	Czech Science Foundation (GACR), <i>Smart systems based on modified graphene oxide particles</i> . GJ16-20361Y
Member of research team	2017	Internal Grant Agency of TBU in Zlín, <i>Evaluation of Carbon-Based Nano-Additives' Influence on Magnetorheological</i>

Performance and Preparation of Electrorheological Suspension with Enhanced Sedimentation Stability, IGA/CPS/2017/004

Principal investigator	2016	Internal Grant Agency of TBU in Zlín, <i>Optimization of viscoelastic properties of polyolefin blends intended for preparation of foams with controlled inner structure, IGA/CPS/2016/009</i>
Member of research team	2014-2016	National Priorities Research Program (NPRP), <i>Preparation, characterization and application of lectin biochips in cancer diagnosis and in discovery of cancer biomarkers, NPRP 6-381-1-078</i>

Josef Osička

Composite materials with photo-responsive capability

Kompozitní materiály s fotocitlivou odezvou

Doctoral thesis summary

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