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# Thermoplastic Elastomers with Photo-actuating Properties

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Additional information is available at the end of the chapter

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## Abstract

This contribution reviews elastomeric materials with photo-actuation behavior with emphasis on thermoplastic elastomers and their composites. The principles of the photo-actuation and the main factors affecting the photo-actuation phenomena of thermoplastic elastomer materials are discussed in detail. The well-performing photo-actuating systems involving both statistical and block copolymers-based thermoplastic elastomers are assessed in terms of their advantages and limitations. Methods for evaluation of photo-actuation behavior of the materials are reported as well. Finally, the utilization of the photo-actuating thermoplastic elastomers is presented.

**Keywords:** Thermoplastic polyurethane, styrene-isoprene-styrene, carbon nanotubes, graphene, liquid crystals

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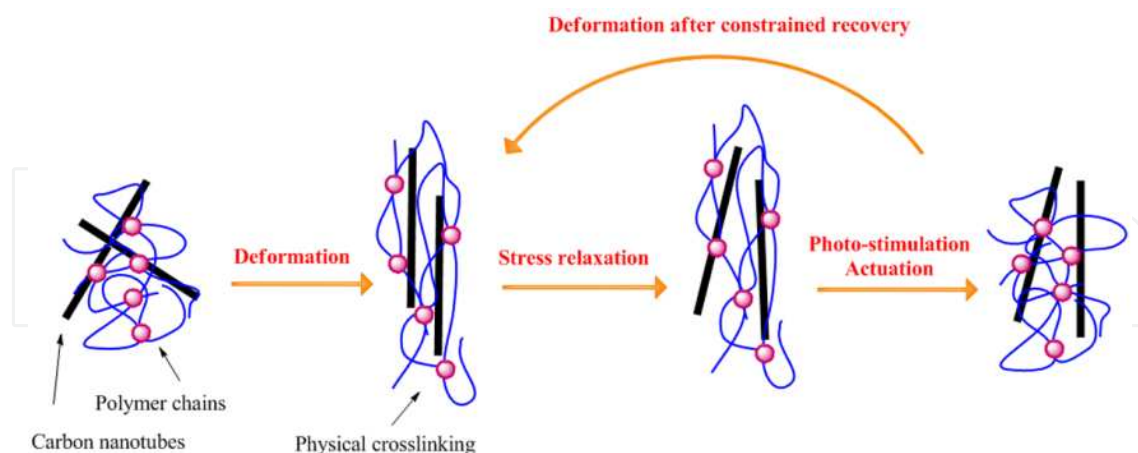
## 1. Introduction

MERGEFORMAT Actuation phenomenon is considered as a material's ability to undergo reversible shape changes in response to an external stimulus [1–3]. There are several trigger stimuli reported, such as the electric field, light, pH, or temperature [4–8]. The trigger-responsive materials find their employment in a wide range of applications comprising sensor, artificial muscles, etc. [1, 2]. Photo-induced actuation technologies can offer many advantages over traditional, mainly electrically driven, actuators, such as remote energy transfer, remote controllability, better scalability, low electromagnetic noise, easy construction, and capability

of working in harsh environments [7]. Generally, the actuating materials can be pure polymers or polymer composites. In both cases, the energy absorber-triggers and assembling structures need to be present in the materials [2]. However, the actuation may be improved by the addition of an energy trigger. As an energy absorbers, dyes [9] or carbon based fillers were reported [10, 11].

Various elastomers were investigated for their photo-actuation behavior, including liquid crystalline elastomers, poly(dimethylsiloxane), various thermoplastic elastomers (TPEs) based on polyurethane, poly(ethylene-co-vinyl acetate) (EVA), polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), and acrylic-based block copolymers, as well as hydrophilic copolymers such as NAFION or hydrogels based on copolymers of acrylic acid and *N*-isopropyl acrylamide. The principles of photo-actuation depend on the type of elastomer and type of the light absorbers.

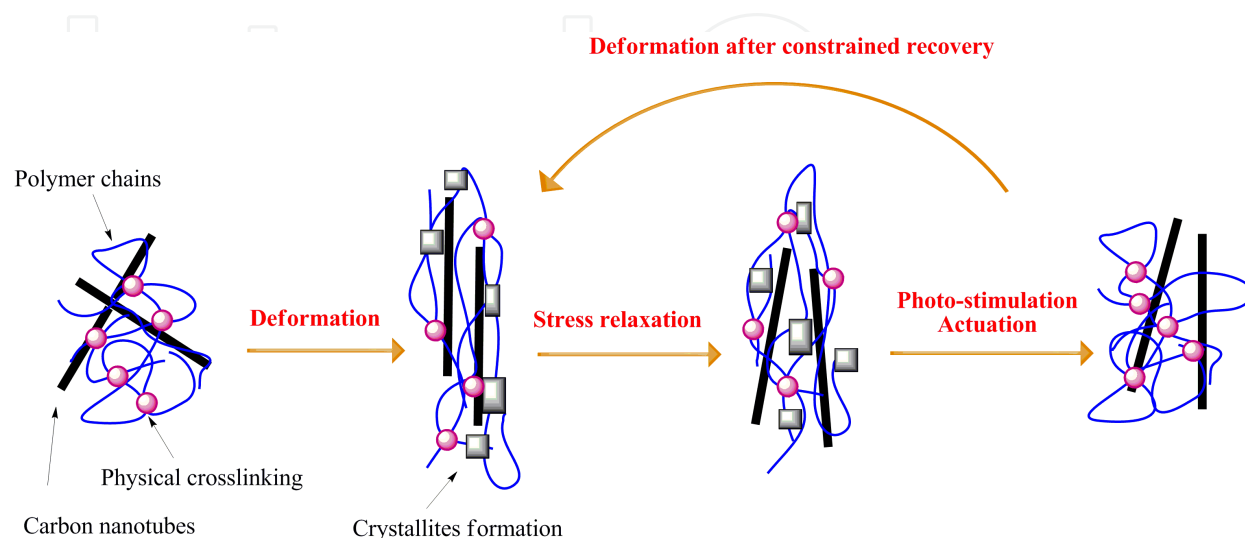
The most common principle of photo-actuation of chemically cross-linked elastomers and/or TPEs is based on the presence of soft segments responsible for shape changes under illumination, and hard segments responsible for returning the material to its stage before illumination [12]. Thus, the pre-strained material containing some light absorbers absorbs the energy from the light and converts it to heat that is conducted through the material. 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 (Figure 1). The hard segments are formed from chemically or physically cross-linked parts, enabling the reversibility of the actuation by the energy balance between absorbed and released energy in the form of mechanical response. Therefore, sometimes the term photo-mechanical actuation is also used for the photo-actuation phenomenon [13].



**Figure 1.** Principle of photo-actuation behavior of physically or chemically cross-linked systems.

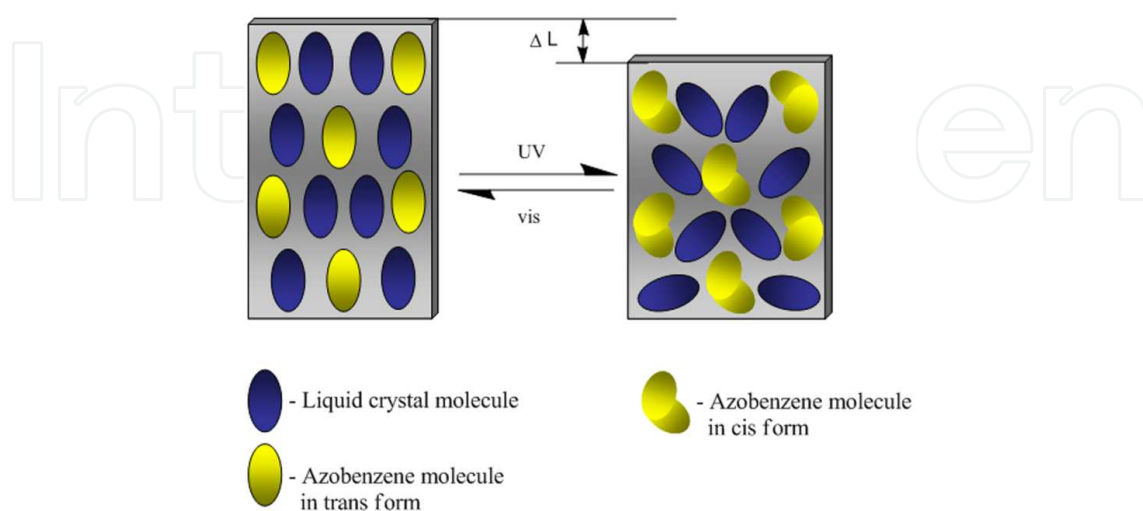
Thermoplastic polyurethanes (TPUs) materials have unique basis of the photo-actuation phenomenon. Depending on the chemical composition, the polymer chains consist of soft segments with melting point ranging from 35°C to 50°C and hard segments with melting point exceeding 100°C. During application of certain pre-strain to the material, the soft polymer

chains are crystallized (Figure 2). These crystallites provide additional physical cross-linking that stabilize the polymer chains in elongated state. The actuation occurs after melting the soft crystallized segments as a recoiling of the soft polymer segments. In case of light induced actuation, the energy from the light source transported to the polymer chains must be high enough to reach the melting point of the soft segments [12].



**Figure 2.** Principle of photo-actuation behavior of thermoplastic polyurethanes [12].

The main principle of the photo-actuation of liquid crystals and liquid crystalline elastomers is based on the ordering and disordering of the structure upon light stimulation (Figure 3) [14–16]. The material is able to be reversibly transformed between these two phases as a result of stimulation, while actuation stress is created. The magnitude of the shape changes and the stress development are strongly influenced by various factors, such as toughness of the polymer matrix, modification of the polymer matrix, or type of additive.



**Figure 3.** Principle of photo-actuation behavior of liquid crystals systems [14].

Very rare photo-actuating principle was found on the hydrogel samples [17]. In this case the actuation principle is based on the difference of swelling in the dark and upon the light and will be described more in detail later. Such changing of dark/light conditions is not that fast as in case of previous principles; however, the potential applications of such systems are very promising and the preparation of the new materials with shorter response time is highly challenging.

Here the photo-actuation of various systems and their advantages and disadvantages will be reviewed, while photo-actuating systems based on thermoplastic elastomers will be described more in detail. Analytical methods used for determination of photo-actuation behavior of various systems will be discussed as well. Finally the applicability of the photo-actuating TPE will be referred.

## 2. Photo-actuation of chemically cross-linked elastomers

### 2.1. Liquid crystal elastomers

Liquid crystals (LCs) are the most common materials frequently applied in order to provide the system with good actuation behavior [18]. This unique property is allowed due to the structure of the LCs that combine the mobility of the isotropic liquids and orientation order of crystalline solid [15]. By incorporation of the light-triggered materials to the LCs, the alignment can be properly controlled over large areas, and thus the materials can be effectively utilized in photonic applications such as signal processing, optical switching, or already mentioned photo-actuation [19–21].

However, it was found out that photo-chemical phase transitions disrupt the LC phase and the material turns to isotropic [16]. Thus, the research interest was further focused on the preparation of the cross-linked LCs structures. Since Finkelmann et al. showed the photo-contraction of liquid crystal elastomers (LCEs) and Ikeda provided the system with photo-actuating LCE films [22], the main aim of the scientific groups has been focused on the preparation of stable and well photo-actuating systems.

The main principle of LCEs utilization is the weak cross-linking of ordered macroscopical structure, which provides the benefits of orientation order of liquid crystals and elasticity of common rubbers [23, 24]. The typical case of cross-linked liquid crystalline network is LCE in the form of uniaxially oriented planar film where the gradient in light intensity through the thickness of the film causes photo-actuation [16, 25–28]. Unfortunately, the response to the external stimulus (light) is rather slow and shape changes are small due to the low thermal conductivity resulting in low energy transfer within the material. This drawback can be solved by the incorporation of light-triggered materials similarly as in the case of LCs, or by addition of fillers improving the thermal diffusivity within the whole final material.

In order to perform the LCEs with excellent photo-mechanically responsive properties, light-sensitive monomer can be used. The final materials containing mainly azobenzene derivatives belong to highly photo-actuating materials [29–31]. This material is unique due to its dynamics

of *trans* to *cis* isomerization of azobenzene unit resulting in the change of absorption spectrum able to report the local rigidity of its surroundings [32]. Thus in ordered liquid crystalline network, *trans-cis* isomerization leads to order reduction resulting in the macroscopic contraction in the main-chain direction and an expansion in the opposite direction. Such systems exhibit considerably improved photo-actuating properties [33].

Another additive, which can considerably improve the photo-actuating properties of the LCEs, are carbon nanotubes (CNTs). CNTs are efficiently applied due to their one-dimensional shape, nanoscale diameters, large surface area, and excellent electrical and thermal properties [34, 35]. Special case of carbon nanotubes effectively applied in photo-actuating systems are single-walled carbon nanotubes (SWCNTs) exhibiting strong absorptions in the visible and near-IR region [36]. Therefore, they efficiently convert the light energy into thermal energy providing the heat source at nanoscale and thus create the thermal pathways within the liquid crystal elastomer upon IR irradiation [37, 38]. However, the utilization of the CNTs in the case of LCEs is rather limited since the proper dispersion of CNTs in case of higher loading (above 1 wt. %) is very difficult especially without surface modification [38, 39]. This drawback can be solved by incorporation of the pyrene to both ends of the LCE chains [40].  $\pi$ - $\pi$  interactions between the pyrene group and CNTs can significantly improve the dispersion of the CNTs in LCEs [38].

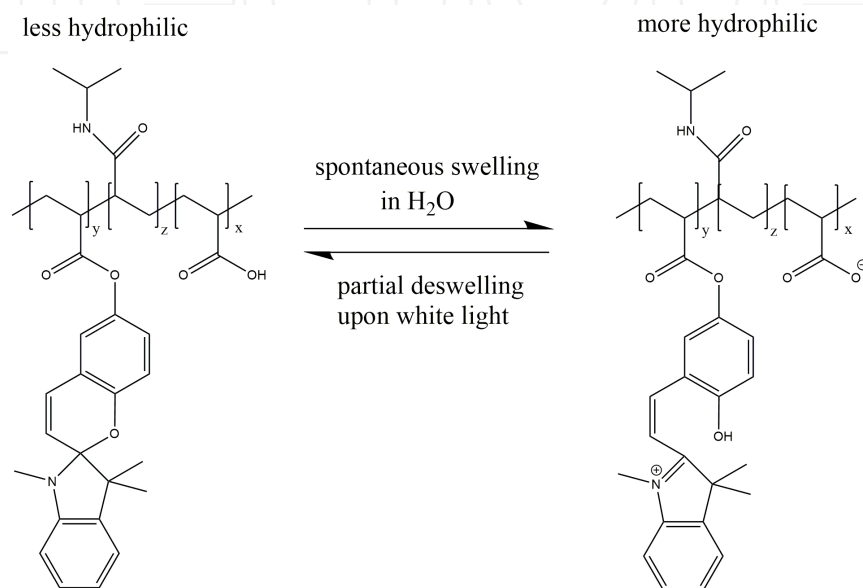
Finally, it can be concluded that from the group of liquid crystals, mainly liquid crystal elastomers are effectively applied due to their excellent physical properties. However, in order to facilitate the photo-mechanical response of those materials, various additives can be efficiently utilized. The additives, such as azobenzene-based derivatives or carbon nanotubes provide better absorption of the light and improve thermal conductivity of the materials.

## 2.2. Other chemically cross-linked elastomers

Poly(dimethyl siloxane) (PDMS), which was often used as a main chain LCE, was effectively used as a matrix also in other systems for photo-actuation applications. This versatile material have many potential applicability in the medical field, due to good biocompatibility, low glass transition temperature, and linear elasticity over broad temperature range (-50°C–200°C) and strains [41]. Solely, PDMS has very poor mechanical response to the light because of low thermal conductivity. Hence, PDMS matrix has to be filled with carbon-based fillers. The composites based on graphene-nanoplatelet were found to exhibit improved thermal conductivity of the samples, and thus also enhanced photo-actuation response [11, 42]. The contraction of the irradiated samples was obtained only above the certain pre-strain (above 10 %). In the case of composites containing thermally reduced graphene oxide, the pre-strain of 9% was sufficient to observe the contraction [7]. Nearly twice higher photo-actuation stress was obtained in comparison with CNTs-containing PDMS composite materials [1, 43, 44]. Thus, PDMS-based materials are very promising for their application as a photo-actuator mainly after the incorporation of the light-triggered fillers such as CNTs or graphene oxide. Those fillers significantly improve the thermal conductivity, resulting in better heat exchange within the material and thus provide the systems with promising photo-actuation performance.

Special photo-actuating materials are based on hydrogels [17]. The hydrogels were made by copolymerization of *N*-isopropyl acrylamide with various ratios of acrylic acid (AA). Benzo-

spiropyran was used as an energy absorber in this system. The swelling of the samples in water changed with switching on/off the light. When the samples were exposed to the light the relative gel swelling was 78 %, while after switching off the light, the relative gel swelling increased up to 96%. This photo-actuation behavior was stable up to five light-dark cycles. This unique property is mainly caused by the utilization of the AA enhancing the proton transfer within the sample when exposed to light or dark and improving the swelling/contraction behavior (Figure 4).



**Figure 4.** Schematic representation of the proton exchange taking place in hydrogels between the acrylic acid and the benzospiropyran in the dark and under irradiation [17].

### 3. Photo-actuation of thermoplastic elastomers

TPEs having physically cross-linked structure possess several advantages compared with chemically cross-linked elastomers. The main advantages are a repeatable processability of TPEs and possibility of tuning their mechanical properties by choosing the different segments to tailor finely the required properties. TPEs are also relatively cheap compared with liquid crystal-based systems. Therefore, the TPE systems are very promising not only from laboratory or specified purposes point of view, but also in terms of large-scale industrial application.

All of the TPE photo-actuating systems utilize light-triggered additives, mainly carbon-based particles, in order to enhance their photo-actuation response [45–47]. However, the poor dispersibility of the additives is a common problem. If the light-triggered additive is not well dispersed, the photo-actuation response will be of low performance. Nevertheless, this drawback can be effectively solved by suitable surface modification either covalent [48] or non-covalent [49].

### 3.1. Poly(ethylene-co-vinyl acetate)

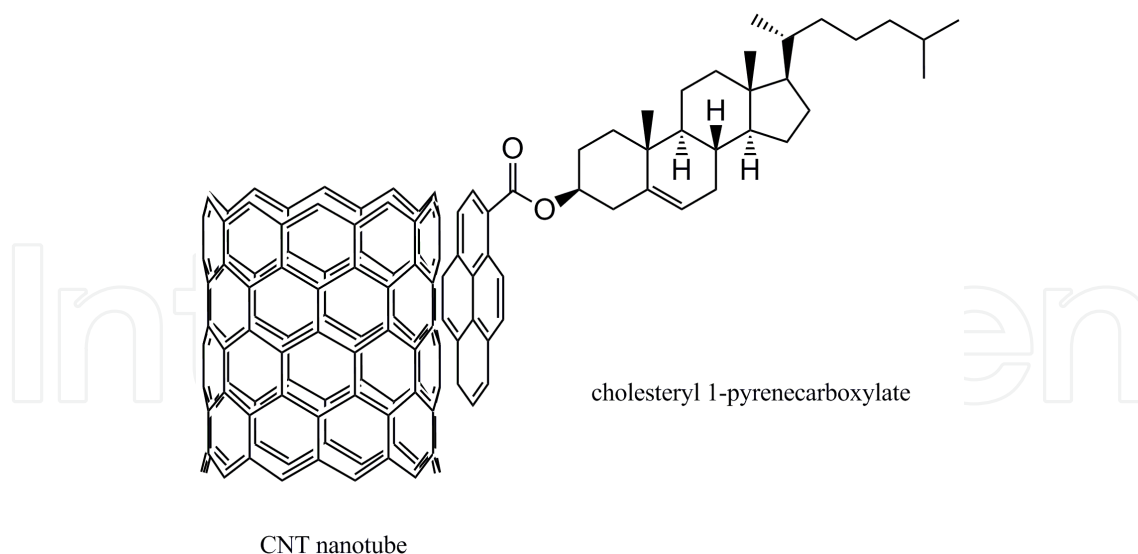
One of the statistical copolymers studied for its photo-actuation properties is poly(ethylene-co-vinyl acetate) (EVA). The ethylene units in EVA provide for semi-crystalline properties of the copolymer, while the vinyl acetate units form amorphous part. The copolymerization of ethylene with vinyl acetate enhances the crystallization of the ethylene units and the crystallization degree of ethylene units increases with increasing amount of vinyl acetate in the copolymer. The final copolymer structure includes two segments: hard segment consisting of ethylene crystalline phase and soft segments represented by amorphous vinyl acetate and amorphous ethylene phase. Thanks to this unique behavior, EVA copolymers provide the materials with tunable elasticity depending on the vinyl acetate content.

The photo-actuation phenomenon has been studied on two EVA copolymers, EVATAN and LEVAPREN 500, with different content of vinyl acetate (28% and 50%, respectively) [47, 50, 51]. Generally, the selection of EVA with appropriate content of vinyl acetate can be crucial. EVA with too low vinyl acetate content will have lower melting point and loss of elastic properties can occur during photo-actuation cycles. The reason is the possible melting of the crystalline phase due to local overheating of the material after absorption of the light by carbon fillers and the release of the energy to the material in the form of the heat. On the other hand, EVA with too high vinyl acetate content can be too tough to provide good photo-actuation.

The effect of the different type of carbon-based fillers such as MWCNTs and SWCNTs and their content in the EVATAN matrix has been investigated. In order to improve the dispersity of the CNTs within the matrix the surface of CNTs was non-covalently modified with cholesteryl 1-pyrenecarboxylate (PyChol), based on  $\pi$ - $\pi$  interactions between CNT surface and pyrene (Figure 5). The EVA composite containing PyChol-modified MWCNTs exhibited higher values of photo-actuation stress compared with PyChol-modified SWCNTs (Figure 5). Better light absorption of the MWCNTs enhancing the photo-mechanical response of the EVA copolymer was suggested as a possible explanation. It has also been found that MWCNT/EVA systems with 0.1 wt. % of PyChol-modified MWCNTs exhibited higher photo-actuation stress compared with the system containing 3 wt. % of PyChol-modified SWCNTs. Even though the authors did not comment on this result, the possible explanation could be that the elasticity of the CNTs/EVA systems is decreased at higher content of the filler, thus suppressing the possibility of this material actuate effectively upon light stimulation.

Similarly, incorporation of 0.1 wt. % of PyChol-modified MWCNTs into the LEVAPREN matrix provided well-dispersed systems with appropriate photo-actuation behavior upon light stimulus [51]. This study was mainly focused on the possibility of the material to provide the system with repeatable photo-actuation phenomenon. In addition the response of this material on various light intensities has been investigated. It has been shown that increasing the intensity of the light led to more pronounced changes but with slower response on the switching on/off the light.

Different methods were used for investigation of photo-actuation behavior of the systems based on EVATAN and LEVAPREN matrices; therefore, the effect of EVA matrix composition cannot be directly compared. Generally, it has been shown that both investigated EVA matrices



**Figure 5.** Schematic illustration of non-covalent modification of CNT with cholesteryl 1-pyrenecarboxylate [50].

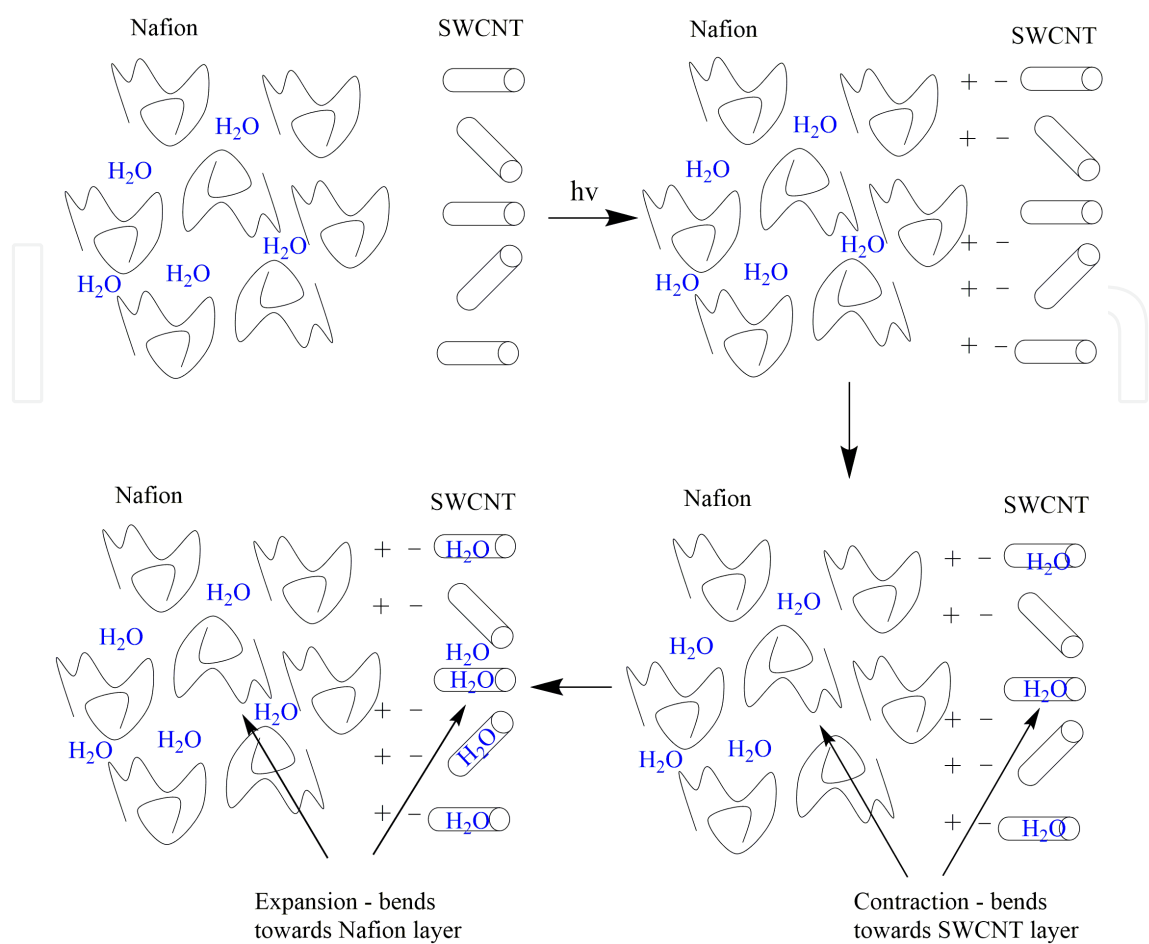
can be utilized for photo-actuation applications, while at least for LEVAPREN, i.e., matrix with higher melting point ( $T_m = 96^\circ\text{C}$  and  $71^\circ\text{C}$  for LEVAPREN and EVATAN, respectively), also repeatable photo-actuation behavior has been proved.

### 3.2. NAFION

Perfluorosulfonated ionomer NAFION is another statistical copolymer with properties of TPEs that has been investigated for its applicability as photo-actuating material [52, 53]. NAFION solely exhibits only poor ability of photo to mechanical energy conversion. Hence, SWCNTs were used as the light-triggered material for preparation of SWCNTs/NAFION bilayer samples providing the good photo to mechanical energy conversion. The determined actuation changes in light switching on/off cycles were  $200\ \mu\text{m}$  and  $600\ \mu\text{m}$  at light intensity of  $18\ \text{mW cm}^{-2}$  and  $75\ \text{mW cm}^{-2}$ , respectively. In SWCNTs/NAFION bilayer system, the photo-actuation phenomenon is obtained by redistribution of the hydrogen ions and water molecules in the SWCNTs/NAFION interfacial region. The light establishes an electric field at the interface that promotes the hydrated hydrogen ions toward the interface. Both the SWCNTs and NAFION contribute to the mechanical action, because water molecules are depleted in the pores of NAFION near the interface and they occupy the interior of the SWCNTs leading to improved effect of contraction of the interfacial region between the SWCNTs and NAFION (Figure 6) [52].

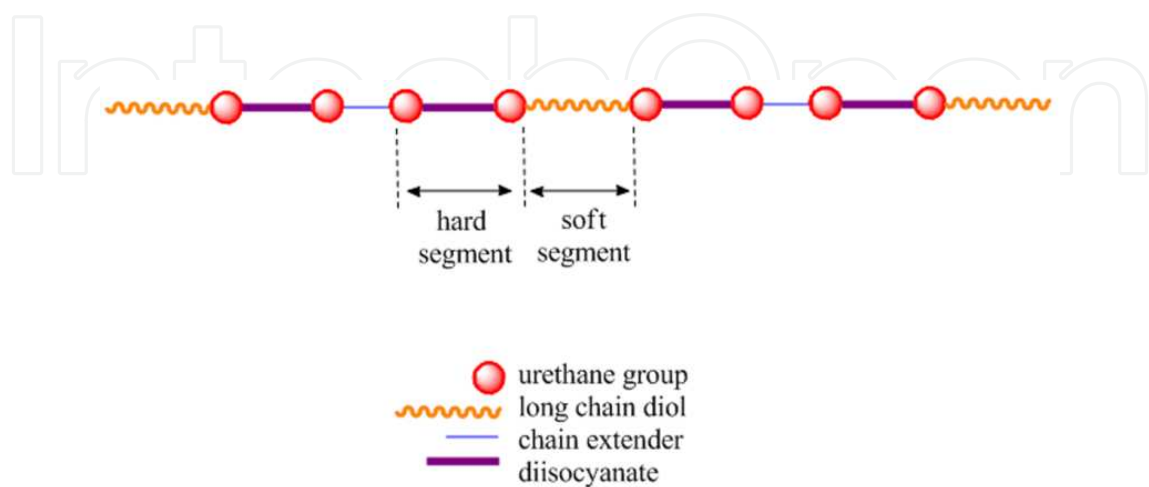
### 3.3. Thermoplastic polyurethanes

TPUs are special type of copolymers, where the hard and soft segments are repeatedly alternating. The hard polymer segments are represented by diisocyanates [54], such as 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI), etc. On the other hand, the soft segments are mainly represented by polyesters [55] or polyethers [56]. However, the real composition of the TPUs usually also includes chain extenders [57] as can be seen in Figure 7. The chain extender is mainly based



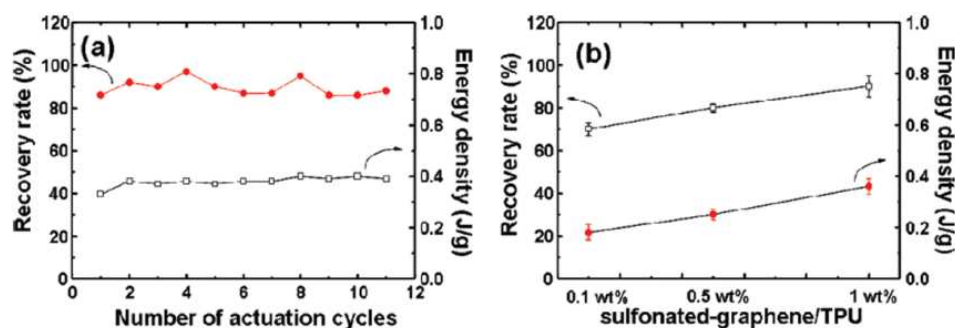
**Figure 6.** Photo-actuation mechanism of the Nafion-SWCNT bilayer upon light stimulation [52].

on linear diols, such as ethylene glycol, 1,4 butadiene, 1,6 hexandiol, etc. This unique composition of the TPUs enable tunability of the mechanical properties and therefore TPUs are very promising material for the photo-mechanical actuation.



**Figure 7.** Composition of the thermoplastic polyurethane elastomers containing chain extenders.

Similar to the previous matrices, TPUs solely exhibit only moderate photo-actuation performance. This is mainly due to poor strain-induced crystallization of the soft segments upon tensile deformation. Hence, all research groups have focused their investigations on the effect of the fillers addition on the strain-induced crystallization of the soft segments upon tension and its connection with the photo-actuation performance of the TPUs composites [12, 58–60]. An impact of the CNTs (5 wt. %) and carbon black (5–20 wt. %) on the mechanical properties, strain-induced crystallization and final photo-actuation performance of TPU (Irogran PS455-203) composites has been investigated (Figure 8) [12]. For the CNT reinforced matrix the young modulus increased by factor 2–5 and considerably improved strain-induced crystallization was observed by DSC and proved by XRD measurements upon tension. Recovery of TPUs composite containing 5 wt. % carbon black, actuated by infrared (IR), was only 25%–30% of the stress achieved by heat actuation, compared to the almost 100% for CNTs containing TPUs composites. Four times higher amount of carbon black (20 wt. %) compared with CNTs (5 wt. %) was needed to obtain comparable deformation of TPU samples under IR irradiation.

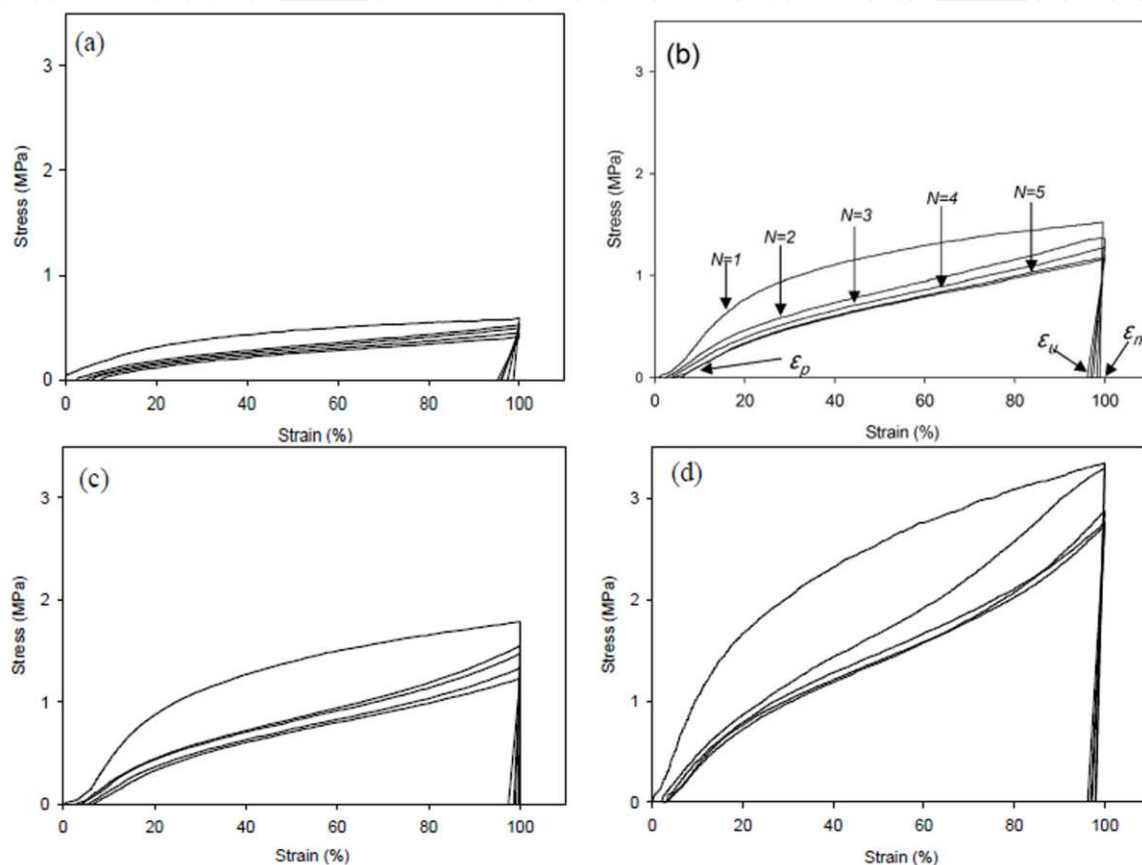


**Figure 8.** The recovery rate for the samples containing SRGO particles. Reprinted with permission from Liang JJ, Xu YF, Huang Y, Zhang L, Wang Y, Ma YF, et al. Infrared-Triggered Actuators from Graphene-Based Nanocomposites. *Journal of Physical Chemistry C*. 2009;113(22):9921-7. Copyright © 2009 American Chemical Society [58].

It has been reported that well-dispersed graphene in MDI-based TPUs provided the system with enhanced strain-induced crystallization, while the poor dispersity of the same graphene in HDI-based TPUs led to the suppressed strain-induced crystallization [59]. Better dispersity of graphene in MDI-based TPUs compared with HDI-based TPUs was attributed to  $\pi$ - $\pi$  interactions between graphene and aromatic ring of MDI. Further improvement of compatibility between graphene and TPUs was obtained after surface modification of graphene. Increasing amount of hydroxyl groups on graphene surface by modification with methanol allowed incorporation of graphene in TPUs structure [59, 61, 62]. Such grafting of TPUs on graphene improved shape recovery (Figure 8). Contrary that it has been shown that intimately mixed graphene disturbed hydrogen bonds between hard segments of SPU balancing the reinforcing effect of graphene. The photo-actuation phenomenon of these systems has been investigated upon IR irradiation and the shape recovery after IR stimulation ranged 90%–99% of deformation.

Influence of the sulfonation of reduced graphene oxide (SRGO) (1 wt. %) on mechanical, energy-transfer and photo-actuation performance of TPU-based (Irogran PS455-203) compo-

sites has been investigated as well [58]. The composite sample containing SRGO exhibited highest absorption in IR region (500 nm - 1000 nm) compared to neat TPU matrix and composites containing 1 wt. % of isocyanated-graphene oxide and reduced graphene oxide. The reason is considerably restored  $sp^2$  network in SRGO. Due to the increased IR absorption, the sulfonated SRGO/TPUs composites contracted faster than others and also the recovery rate was 15% faster compared with isocyanate-graphene oxide or reduced graphene oxide composites (Figure 9).



**Figure 9.** Photo-actuation behavior of the sample (a) pure TPU, (b) TPU with 5 wt. % GO, (c) TPU with 10 wt. % GO, and (d) TPU with 20 wt. % GO [59].

In order to obtain high actuation performance, structural uniformity, good dispersion, and high purity of carbon fillers is crucial. Properties of the carbon fillers are affected by surface defects, large bundles, impurities, the anisotropy, and a structural mixture [63]. Surface functionalization of graphene in order to obtain their good dispersion in polymer matrix results in the decrease in thermal conductivity due to structural defects [64, 65]. Therefore, a balance between the restoration of  $sp^2$  network and the dispersion of graphene is crucial for sufficient reinforcement and high thermal conductivity. Several studies have shown enhanced thermal conductivity and mechanical strength of polymer composites when hybrid graphene/CNT nanofiller were used. The synergistic effect between well-dispersed graphene and CNTs can be tuned by weight ratio of graphene to CNT [66–70]. Expected enhancing of thermal

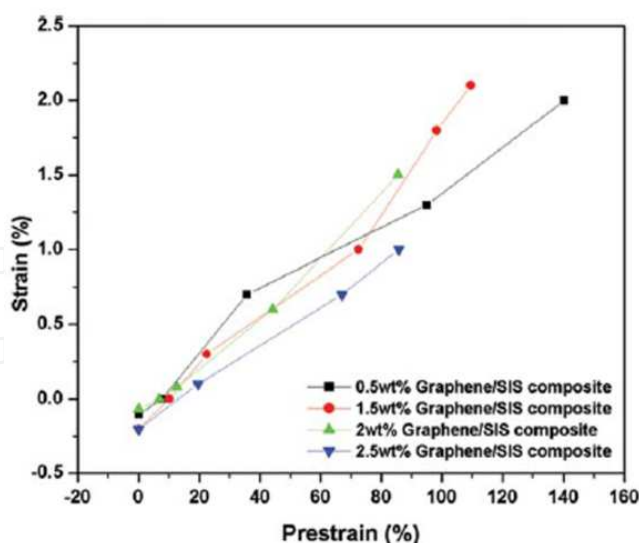
conductivity led to the investigation of the influence of incorporation of various contents of sulfonated CNTs into the SRGO/TPUs composites on photo-actuation performance of the prepared composites [60]. IR absorption of sulfonated CNT/SRGO/TPUs composites was higher than SRGO/TPUs. The DSC results showed that the melting range of soft segment crystallites was shifted to higher temperatures with incorporation of the fillers. This temperature increase was ascribed to the heterogeneous nucleating effect of SRGO and CNT. As expected, all sulfonated CNT/SRGO/TPUs composites exhibited enhanced thermal conductivity. TPUs composite with sulfonated CNT/SRGO ratio of 1/3 showed the best IR-actuated stress recovery of lifting in 18 s. Remarkable IR-actuated recovery delivered the mechanical stress of 1.2 MPa assigned to thermal conductivity of 1.473 W/mK and Young's modulus of 23.4 MPa. It has been concluded that a trade-off between the stiffness and efficient heat transfer, which can be controlled by synergistic effect between SRGO and SCNT, is critical for high mechanical power output of IR triggered actuators. Therefore, SRGO/SCNT/TPUs composites combining high output forces, and good cycling stability are highly suitable for development of advanced photo-actuating systems.

### 3.4. Polystyrene-based block copolymers

The materials investigating for effective respond to the photo-stimulation include also A-B-A triblock-based TPEs. They consist of one polymer block with low glass transition temperature ( $T_g$ ) providing the actuation of the material and two blocks with high  $T_g$  providing the elasticity and reversible shape change after switching off the light stimulus. Mechanical, and thus also the photo-actuation properties of A-B-A triblock-based TPEs can be finely tuned by choice of the monomers structure and ratio between the soft and hard blocks. Similarly, as in all previous cases, the light-triggered materials have to be added to provide the system with sufficient actuation performance. The main A-B-A triblock-based TPE investigated for photo-actuation is polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymer [39, 46, 71].

A reduced graphene oxide (rGO) has been successfully used as a light-triggered material in the SIS matrix [71]. Investigation of the effect of the filler content on the photo-actuation showed that the best performance was obtained for the nanocomposites containing 1.5 wt. % of rGO. The higher rGO content resulted in decreased response that was in consistence with change in the mechanical properties. Apparently, a creep has been observed during irradiation that is understandable with respect to extremely large pre-strain (up to 150%) and also due to the utilization of light source with 22 W cm<sup>-2</sup> intensity, which could significantly contribute to the mentioned creep behavior.

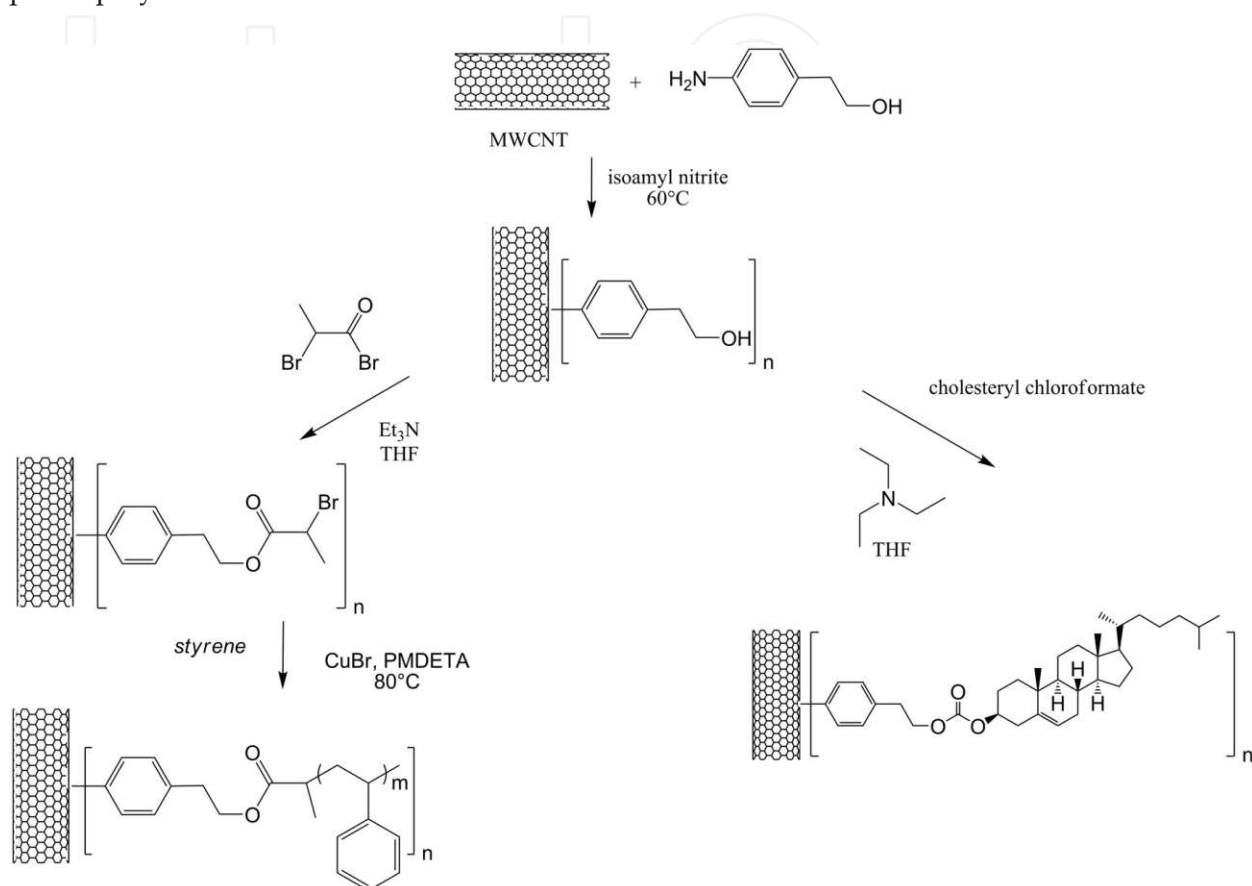
Besides rGO, the MWCNTs have been investigated in SIS matrix as well. Both elongation and contraction were observed under irradiation depending on the applied pre-strain (Figure 10). Under light intensity of 1.5 W cm<sup>-2</sup>, minimal 20% pre-strain was needed to obtain 0.2% contraction of the composite [39]. The highest actuation was obtained at 40% pre-strain with 1.1% contraction. It should be mentioned that the MWCNTs were used in very low concentration (0.01 wt. %). Too high loading of neat MWCNTs disturbs physical cross-linking due to preferential interactions of MWCNTs with polystyrene blocks.



**Figure 10.** Photoactuation behavior of SIS samples with various contents of graphene particles. Reprinted with permission from Ansari S, Neelanchery MM, Ushus D. Graphene/Poly(styrene-*b*-isoprene-*b*-styrene) Nanocomposite Optical Actuators. *Journal of Applied Polymer Science*. 2013;130(6):3902-8. Copyright © 2013 Wiley Periodicals, Inc. [71].

In order to prevent the negative interactions of CNTs with SIS matrix resulted in deteriorating of the mechanical properties, the surface of CNTs was modified. Complex investigation of the structural, mechanical, and photo-actuation performance of CNT/SIS composites with both neat MWCNTs and covalently modified MWCNTs has been reported for filler loading of 0.15 wt. % to 3 wt. % [46, 72]. In order to tailor preferential interactions of MWCNTs with individual blocks of SIS matrix, the surface of MWCNTs was modified either with cholesteryl groups or with short polystyrene chains (Figure 11). In the former case the preferential interactions with polyisoprene phase, and in later case the preferential interactions with polystyrene phase were expected. The dynamic mechanical analysis (DMA) in wide temperature range (from -100°C to 150°C) has been used to investigate the specific interactions of selectively modified carbon nanotubes with individual blocks of SIS. The shift in  $T_g$  and activation energy of glass transition was compared. Addition of neat MWCNT resulted in the shift of  $T_g$  of both polyisoprene and polystyrene phase to lower temperatures, while the influence was more pronounced for polystyrene phase. The cholesteryl-modified MWCNT shifted the  $T_g$  of both polyisoprene and polystyrene phases to higher temperatures, while the shift for polyisoprene phase was more significant. The highest shift in  $T_g$  of polystyrene phase was observed in composites containing polystyrene-modified MWCNTs. Contrary to neat MWCNTs, in the case of polystyrene-modified MWCNTs the  $T_g$  shifted to higher temperatures. The activation energies of glass transitions followed a similar trend (see Table 1). In all investigated composites, an increase of MWCNTs concentration from 1 wt. % to 3 wt. % led to the deterioration of the mechanical properties. The highest actuation stresses were generated by composite containing low content of neat MWCNTs. However, the photo-actuation was irregular and fast drop of the baseline was observed as a result of negative interactions of neat MWCNTs with polystyrene phase and loss of the elastic properties. The most stable and reversible response was obtained in composite containing polystyrene-modified MWCNTs (Figure 12). In this case, however, the actuation stresses were only half of the stresses obtained for composites containing either neat

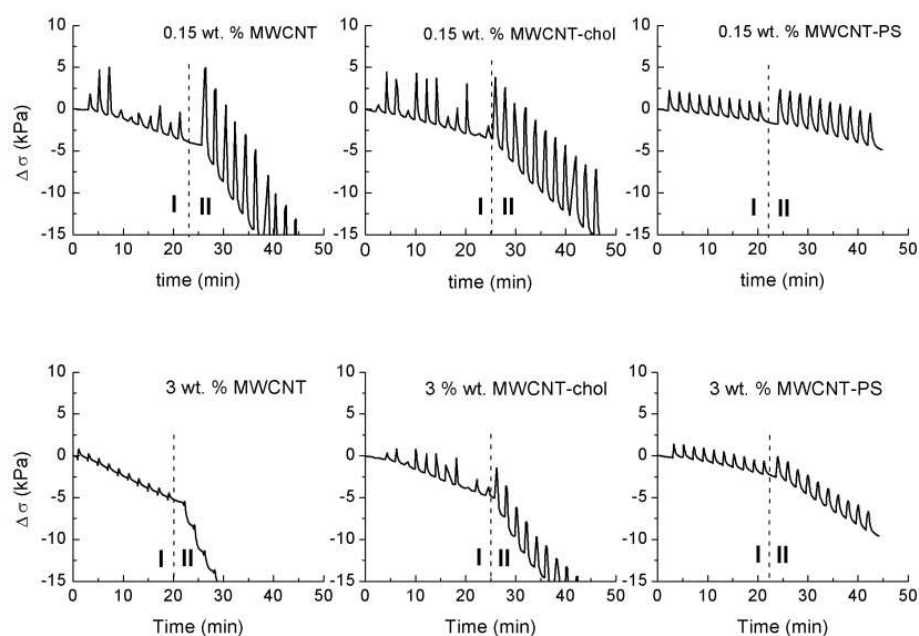
MWCNTs or cholesteryl-modified MWCNTs [72]. The reason is not effective energy transfer from polystyrene-modified MWCNTs, preferentially localized in hard polystyrene phase, to soft polyisoprene phase responsible for actuation changes. These extensive studies showed that the best photo-actuation could be expected in the case of selective localization of MWCNT in the soft phase of triblock thermoplastic elastomers with effective energy transfer only to soft phase polymer chains.



**Figure 11.** Covalent modification of multiwalled carbon nanotubes either by cholesteryl groups or with polystyrene chains [72].

In order to investigate the MWCNTs/SIS composites for their applicability in tactile displays, the Braille-like elements were prepared by thermoforming and their photo-actuation behavior has been investigated [46, 47]. In all experiments, blister expansion was observed as a result of low pre-strain induced during the thermoforming process. Regardless, the actuating response increased with intensity of the light source. The fastest response was observed in the composites containing polystyrene-grafted carbon nanotubes.

Another polystyrene-based triblock copolymer investigated for its photo-actuation properties is polystyrene-*block*-poly(vinylmethylsiloxane)-*block*-polystyrene triblock copolymer [45]. In order to introduce light triggered groups into the matrix, the poly(vinylmethylsiloxane) block was covalently modified by attaching of the pendant azobenzene groups (Figure 13). This material exhibited two  $T_g$  ( $23^\circ\text{C}$  and  $100^\circ\text{C}$  for azobenzene-modified silane block and polystyrene block, respectively). Such narrow difference between the  $T_g$  provides very narrow

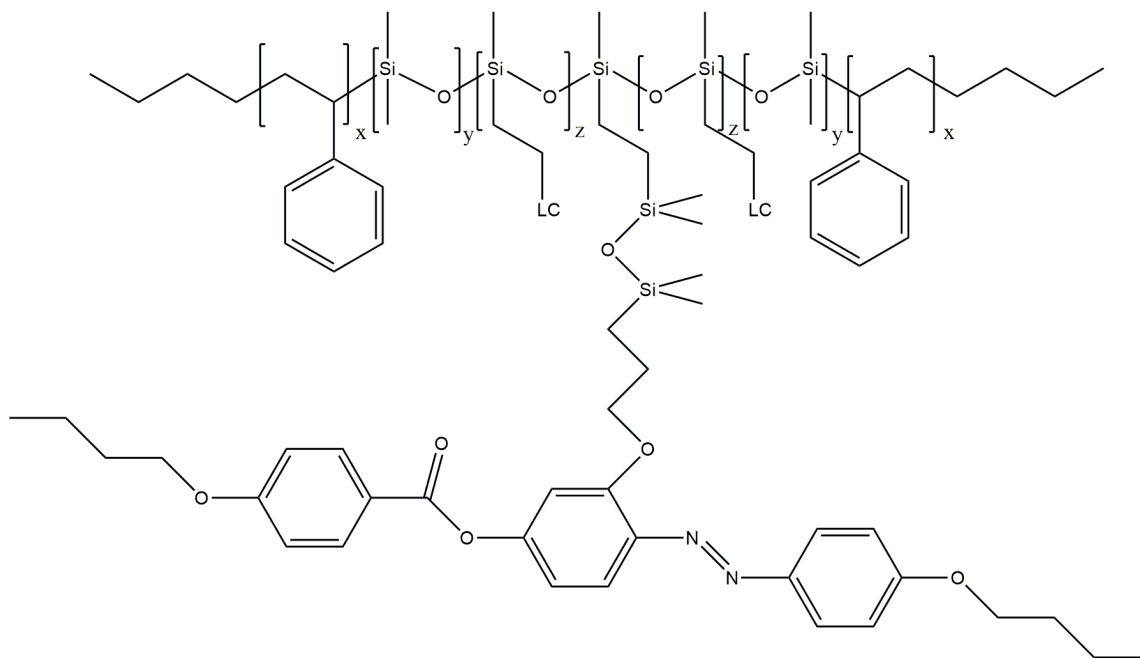


**Figure 12.** Changes in photo-actuation stress for composites containing either 0.15 wt. % or 3 wt. % of neat MWCNT or cholesteryl-modified multiwalled carbon nanotubes (MWCNT) (MWCNT-chol) or polystyrene-modified MWCNT (MWCNT-PS) during irradiation for 10 s (region I) and for 30 s (region II). Reprinted with permission from Ilcikova M, Mosnacek J, Mrlik M, Sedlacek T, Csomorova K, Czanikova K, et al. Influence of surface modification of carbon nanotubes on interactions with polystyrene-*b*-polyisoprene-*b*-polystyrene matrix and its photo-actuation properties. *Polymers for Advanced Technologies*. 2014;25(11):1293-300. Copyright © 2014 John Wiley & Sons, Ltd. [72].

Matrix / Filler	T <sub>g</sub> (°C)				E <sub>a</sub> (kJ/mol)
	soft phase / hard phase				soft/hard phase
	0.5 Hz	1 Hz	2.5 Hz	5 Hz	
Pure SIS	-50.5 / 110.3	-48.7 / 111.1	-46.4 / 112.8	-45.0 / 116.2	174 / 475
SIS / MWCNT	-51.7 / 102.8	-49.0 / 105.5	-47.8 / 109.9	-46.5 / 111.8	186 / 310
SIS/ MWCNT-chol	-47.8 / 110.3	-47.0 / 110.7	-45.0 / 115.2	-44.0 / 117.1	250 / 348
SIS/ MWCNT-PS	-50.4 / 111.8	-48.6 / 112.6	-46.4 / 114.3	-45.5 / 116.1	191 / 650
Pure MBM	-35.5 / NA	-33.7 / NA	-31.3 / NA	-29.5 / NA	184 / NA
MBM/MWCNT	-34.1 / NA	-33.3 / NA	-30.9 / NA	-25.9 / NA	196 / NA
MBM/ MWCNT-g-PBA	-34.0 / NA	-30.8 / NA	-27.3 / NA	-25.8 / NA	209 / NA
MBM/ MWCNT-g-PBA- <i>b</i> -PMMA	-30.8 / NA	-28.7 / NA	-27.1 / NA	-25.5 / NA	223 / NA

**Table 1.** Glass transition temperatures ( $T_g$ ), obtained at various frequencies from DMA measurements and corresponding calculated activation energies of glass transitions of individual phases for pure polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) and pure poly(methyl methacrylate)- *block*-poly(butyl acrylate)-*block*-poly(methyl methacrylate) (MBM) matrices and their composites containing 1 wt. % of neat or modified MWCNTs. NA stays for Not Available, since  $T_g$  of PMMA phase was not observable.

application window for these materials, even though they provide very promising photo-actuation performance with reversible strain of 3.1% and tensile strength 25.7 kPa.



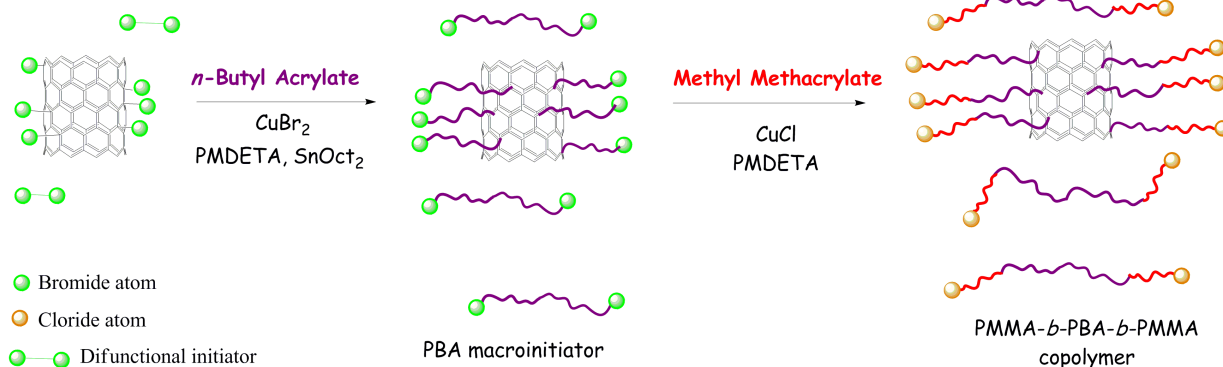
**Figure 13.** Schematic illustration of triblock copolymer TPEs containing pendant azobenzene groups [45].

### 3.5. Acrylic block copolymers

Acrylic-based TPEs are triblock copolymers consisting of one middle soft polyacrylate and two hard polymethacrylate blocks. These materials were just very recently investigated as photo-actuators with very promising results [48, 73]. Their main advantage compared with the styrene-based triblock TPEs is the higher UV stability, better mechanical properties at elevated temperatures, and variability of their properties depending on the choice of (meth)acrylate monomers structure.

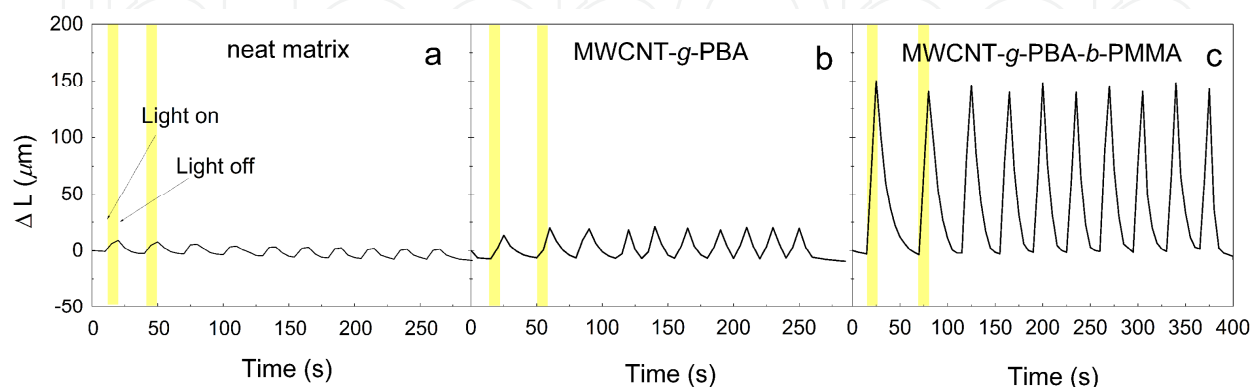
The photo-actuation phenomenon has been investigated on poly(methyl methacrylate)-*block*-poly(butyl acrylate)-*block*-poly(methyl methacrylate) triblock copolymer (PMMA-*b*-PBA-*b*-PMMA) filled with MWCNTs as a light-triggered material. In addition to neat MWCNTs, also MWCNTs grafted with either poly(butyl acrylate) homopolymer (MWCNT-*g*-PBA) or poly(butyl acrylate)-*block*-poly(methyl methacrylate) diblock copolymer (MWCNT-*g*-PBA-*b*-PMMA) have been incorporated into the PMMA-*b*-PBA-*b*-PMMA matrix [48, 73]. The modification of MWCNTs was focused on the improvement of interactions with soft PBA phase, stiffening of the soft phase, and efficient heat transfer from MWCNTs to the soft PBA phase. Composites containing 1 wt. % of neat MWCNTs or MWCNT-*g*-PBA were prepared by solution mixing with polymer matrix, while 1 wt. % MWCNT-*g*-PBA-*b*-PMMA composite was prepared during *in situ* polymerization of PMMA-*b*-PBA-*b*-PMMA matrix (Figure 14) [48]. Therefore, the composites based on PMMA-*b*-PBA-*b*-PMMA containing 1 wt. % MWCNT-*g*-PBA-*b*-PMMA were prepared. It has been proved by electron microscopies that significantly better dispersity with more homogeneous distribution of the MWCNTs was obtained in the

composite prepared *in situ* during polymerization. The modification of MWCNTs led to enhancement of both  $G'$  and  $G''$  in wide range of temperatures (up to 260°C) compared to pure matrix, while the enhancement was most pronounced in the case of MWCNT-g-PBA-b-PMMA composite.



**Figure 14.** Schematic illustration of covalent modification of MWCNT surface with PBA-*b*-PMMA diblock copolymer *in situ* during synthesis of PMMA-*b*-PBA-*b*-PMMA matrix [48].

DMA analysis reveals that the incorporation of neat MWCNTs affected the  $T_g$  of PBA phase only negligibly (-33.3°C compared with -33.7°C for pure matrix). In the MWCNT-g-PBA composite the  $T_g$  increased to -30.8°C and the most pronounced shift was obtained in the case of MWCNT-g-PBA-*b*-PMMA composite (-28.7°C) [73]. The activation energies of glass transition of the PBA phase increased in the same order (see Table 1). Similarly, significantly improved photo-actuation ability was obtained in the case of MWCNT-g-PBA-*b*-PMMA composites (Figure 15). Under all investigated conditions the reversible contraction with the highest absolute values of photo-actuation was observed in this composite. It exhibited the actuation contraction of 280  $\mu\text{m}$  and 400  $\mu\text{m}$  at light power of 6.6 mW and 18.5 mW, respectively, after 30 s of irradiation. These values correspond to 3.2% and 4.5% change in sample length, respectively. Since both MWCNT-g-PBA and MWCNT-g-PBA-*b*-PMMA were found to interact preferentially with soft PBA phase, the big difference between the photo-actuation behavior of these two composites can be assigned to much better dispersity and more homogeneous distribution of the later one resulting in more effective heat transfer to the matrix.

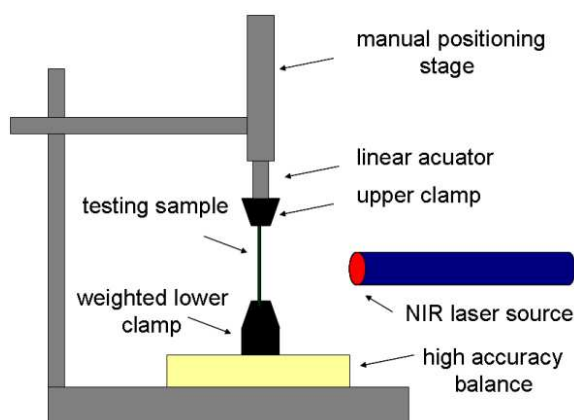


**Figure 15.** Comparison of actuation length change of neat matrix (a), composite containing 1 wt. % of MWCNT-g-PBA (b) and MWCNT-g-PBA-*b*-PMMA (c), pre-load: 0.05N, irradiation for 10 s, light power of 6.6 mW [73].

## 4. Methods for determination of photo-actuation behavior

### 4.1. Setups for measuring of photo-actuation performance

Several different methods have been developed to measure photo-actuation ability of TPE materials. A setup frequently used for the investigation of photo-actuation behavior is the dynamometer [11, 50]. In this case, the sample in the form of the stripe is fixed in the upper holder and in the bottom holder. On the bottom holder, the weight of various values is mounted. Thus, the certain pre-load is applied (Figure 16). The pre-loaded sample is then exposed to photo-stimulation and the change in the length is measured. The main advantage is the relatively easy construction of the setup; however, if the materials with different mechanical properties are subjected to the certain pre-load (depending on used weights), different pre-strain is achieved. Hence, the adjusting to certain pre-strain is rather impossible using various weights. Also, the accuracy of the length change measurement is not precise [11].



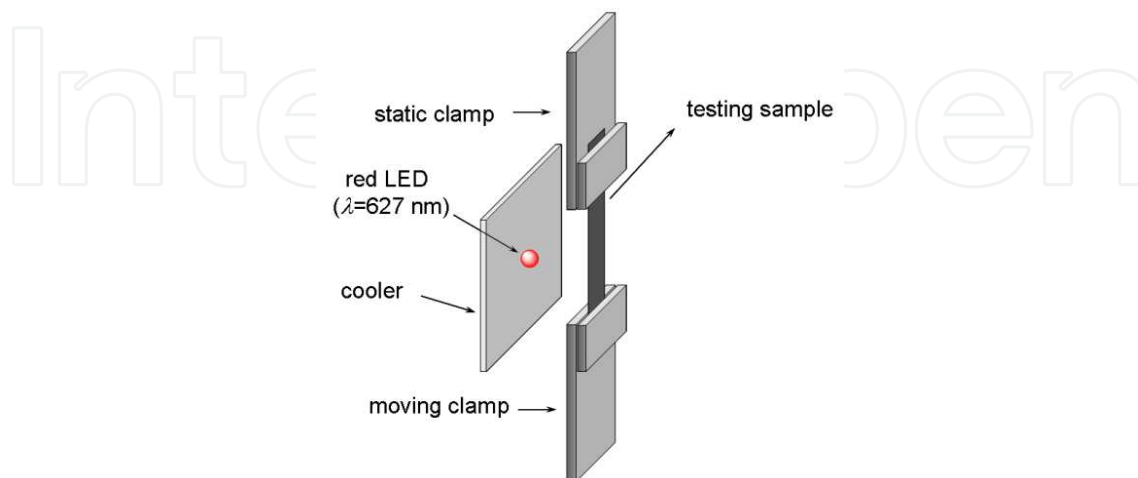
**Figure 16.** Dynamometer setup used for the investigation of photo-actuation behavior [11].

The same principle of applying certain pre-load has been used in the case of samples measured with the thermo-mechanical analyzer (TMA) [48, 73]. 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 nanometers scale.

A very often utilized device for the investigation of photo-actuation behavior of TPE-based actuators in the form of the stripes is the universal tensile testing machine [12]. This machine allows to define a certain level of the pre-strain and thus a certain degree of alignment of polymer chains can be achieved. In the case of TPU samples, strain-induced crystallization also takes place and is fixed. When the material reaches equilibrium, it is able to respond on application of the light stimulus and to exhibit photo-actuation phenomenon [12].

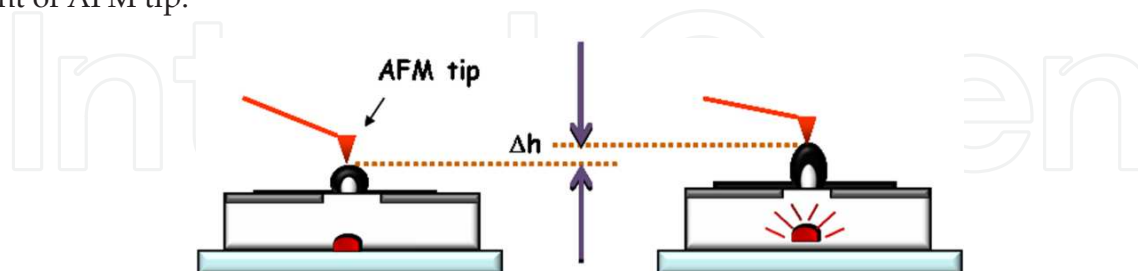
The most precise device for the photo-actuation investigation is dynamic mechanical analysis (DMA) in iso-strain tensile mode (Figure 17) [50, 72]. The sample in the form of the strip is fixed into the clamps and the certain pre-strain is set. After stabilization of sample stress while keeping the same clamp distance, photo-stimulation is started. This device very precisely

calculates the position of the clamps and records the load resulting from the contraction or expansion of the sample. According to these values, the device automatically provides the certain level of the actuation displacement (in the range of  $\mu\text{m}$ ) of the sample, as well as the actuation stress (in the range of kPa) as the most important values for the evaluation of the photo-actuation phenomenon.



**Figure 17.** DMA setup for investigation of the photo-actuation performance [50].

Some photo-actuation studies were performed directly for the possible application of the materials in the development of new types of tactile displays. In these studies, the Braille-like elements were prepared instead of stripes and thus, also, different methods for evaluation of their photoactuation behavior have been developed. Atomic force microscopy (AFM) was one of the utilized devices to detect the movement of the Braille-like element (Figure 18). In this method, the AFM tip is placed on the top of the element and after exposition to the light the AFM records the tip movement up to several  $\mu\text{m}$  [46, 47]. This technique is very useful for the investigation of the photo-actuation kinetics; however, the actuation stress cannot be calculated and the actuation displacement investigation is limited by maximal possible displacement of AFM tip.



**Figure 18.** AFM setup for investigation of the photo-actuation performance of the samples in the form of Braille-like elements.

The second device utilized for the investigation of the Braille-like elements is scanning electron microscopy (SEM) [47, 49]. In this case, the Braille-like element is placed into the SEM evacuated chamber and then the samples are irradiated through the self-modified setup. The maximal change in the Braille-like element height is recorded. Again, this method does not

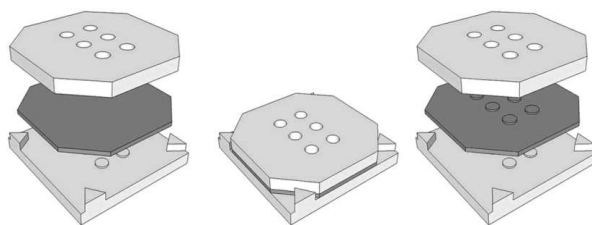
allow the calculation of the actuation stress, but it can provide good information of the Braille-like element photo-actuation performance.

#### 4.2. Preparation of samples for measuring of photo-actuation performance

In most of the set-ups used for the measurement of photo-actuation, the tested samples were in the form of strips. The polymer films for strips can be simply prepared by casting from the solution. However, very often, carbon base fillers are used as light-triggered materials that have to be incorporated into the TPE matrix. In order to provide the photo-actuator with promising behavior, the additive should be well dispersed and homogeneously distributed in the TPE matrix. There were two methods reported for preparation of photo-actuating TPE composites in the literature. The first method is solution mixing, where the filler is dispersed in the proper solvent, while very often the ultrasonication is needed, and TPE matrix is afterwards added to the additive dispersion either in the form of solid or solution. When TPE is added as a solid, the mixture has to be mixed for a sufficiently long time to completely dissolve the matrix [47–51, 72]. Sonication and/or high shear mixing can be applied in order to disperse the filler well [46, 72].

The second method is based on the preparation of *in situ* composites during synthesis of polymer matrix in the presence of a filler [48, 73]. This method allows direct modification of filler surface during the polymerization process and can provide composites with much better dispersed filler. After polymerization, the polymer/filler mixture has to be precipitated to remove unreacted monomer and then re-dispersed in a solvent for casting process. In both methods, finally, the homogenous mixture is casted onto the Teflon dishes or molds of specified shape [50, 51] and the solvent is evaporated at elevated temperature and reduced pressure. Then the samples for photo-actuating investigation is cut to obtain the regular shape of stripes not exceeding dimensions of length 30 mm, width 10 mm, and thickness 1 mm. The thickness of the tested stripes was usually in the range of 0.3 mm–0.8 mm [47–51, 72].

In the case of Braille-like elements, thermoforming using a specific mold was used (Figure 19). Thermoforming allows not only preparation of the sample with required shape, but also obtaining certain pre-strain and orientation of the polymer chains needed for achieving the photo-actuation behavior of the material [46, 47].



**Figure 19.** Thermoforming process of the Braille-like elements. Reprinted with permission from Ilcikova M, Mrlik M, Sedlacek T, Chorvat D, Krupa I, Slouf M, et al. Viscoelastic and photo-actuation studies of composites based on polystyrene-grafted carbon nanotubes and styrene-*b*-isoprene-*b*-styrene block copolymer. *Polymer*. 2014;55(1):211-8. Copyright © 2013 Elsevier Ltd. [46].

## 5. Applicability of photo-actuating TPE materials

The biocompatible grades of TPU open opportunity for utilization of photo-thermal activated actuators for *in vivo* medical applications. One of the proposed actuator was a photo-thermally expandable vascular stent for treatment of arterial stenosis. The polymer-based stents were designed to replace the frequently used metallic stents due to enhanced flexibility and possible drug elution [1]. Engineering aspects related to the application of photo-actuating thermoset TPU as materials for intravascular laser activated devices were reported. There were two type of devices designed. The interventional ischemic stroke devices and micro-grippers based on releasing embolic coils. The crucial parameter of suitable TPU stents was addressed to  $T_g$  that has to be low enough to actuate at the lowest laser power, but it should be high enough not to self-expand at body temperature. The suitable materials were determined as those actuated in the range of 65°C to 80°C. The crucial issue was determined as attaining these temperatures in the actuators in flow conditions and coupling of the light from the diffusing fiber through the blood into the actuator.

Later on, laser actuated intravascular thrombectomy device based on thermoplastic TPU has been designed [2, 3]. The prototype of self-expanding stent was composed of TPU crimped over a light diffuser attached to the end of the optical fiber connected to the IR laser diode [3]. The optical fiber had a dual function, first as a transport vehicle and second as a light energy delivery. The authors used the MM5520 phase separated TPU with  $T_g$ s of -25°C and 55°C. The material was first crimped above  $T_g$ , i.e., above 55°C, and cooled down. The primary shape was achieved after heating the material to 40°C–45 °C. The modulus turned from 800 MPa to 1.4 MPa during the shape change. The requirements for the moduli of the expandable polymer stents lie in the range from 800 MPa to 7 GPa in the glassy state. The applications such as neural stenting require low mechanical strength and the moduli ranges from 400 MPa in the glassy state. However, in this case, the low expansion force is generated [4].

The TPU was considered as a promising candidate for vascular stents, as the requirements for mechanical properties, deployment, and biocompatibility are met. Nevertheless, there are still some aspects to face, such as those related to the prevention of photo-thermally induced injury of arterial tissue.

Recently, the photo-thermally responsive TPEs have been utilized in the development of tactile displays for blind or visually impaired people [5]. The everyday activities of the population of the whole world can be greatly improved with the implementation of at least one Braille-like element in various devices. For wide industrial application, the cost of raw material and processing belong to decisive factors. From this point of view, the TPE poses advantage over still costly LCs or chemically cross-linked elastomers, which were recently studied for the same application as well.

Another potential application in plastic motors has emerged recently [9]. The photo-thermally activated localized contraction of scrolled strip caused rolling of the sample upon irradiation by UV and visible light. The investigated material was based on LCE with aligned structure.

Even though TPE actuators have not been tested in this pioneer publication, it can be assumed that TPEs with oriented structure can be suitable candidates for such application as well. Similarly, even though so far TPE photo-actuators have not been investigated for other applications, these materials that have responses in visible or near-infrared (NIR) wavelength region have various potential applications in telecommunication, thermal imaging, remote sensing, thermal photovoltaics, solar cells, sensors, etc.

## 6. Conclusions

The photo-actuating phenomenon is mostly influenced by the chemical structure of matrix, light absorbers, and fillers improving mechanical properties and thermal conductivity of the final material. Thus, photo-actuating materials with good performance are mostly composites consisting of elastomers and carbon-based fillers. TPEs having physically cross-linked structures possess several advantages compared to chemically cross-linked elastomers. The advantages of TPEs compared to chemically cross-linked elastomers are repeatable processability, tuning their mechanical properties by slight changes in composition and chemical structure, and price. Good photo-actuation response has been shown for TPE composites mainly based on thermoplastic urethanes, poly(ethylene-*co*-vinyl acetate), polystyrene-*block*-polyisoprene-*block*-polystyrene and poly(methyl methacrylate)-*block*-poly(butyl acrylate)-*block*-poly(methyl methacrylate) matrices. Carbon nanotubes and graphene are appropriate fillers providing good optical, mechanical, and thermal properties at quite low loading. Good dispersity and homogeneous distribution of the filler in the TPE matrix is crucial for achieving materials with good photo-actuation behavior. Therefore, surface modification of the fillers to improve compatibility with TPE matrix is encouraged. In block copolymers-based TPEs, preferential interactions of fillers with soft phase should be tailored to maximize the heat energy transfer to the soft phase, which is responsible for the actuation changes of the material. The photo-actuation phenomenon has been utilized in various smart applications. Poly(ethylene-*co*-vinyl acetate) and polystyrene-*block*-polyisoprene-*block*-polystyrene have been used in the development of tactile displays, and the biocompatible thermoplastic polyurethanes have been utilized for fabrication of vascular stents. The applicability of these materials is, however, much broader than published so far.

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