

# Modification of Carbon Nanotubes: Improvement of Physical and Photo-actuating Properties of their Elastomeric Composites

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## I. INTRODUCTION

Carbon nanotubes (CNTs) are very famous species of carbon-based fillers with one-dimensional structure. During the last twenty years many research groups have intensively studied their basic properties and potential applications [1-3]. Their main advantages are very good mechanical properties [4, 5] as well as electrical conductivity [6, 7]. Thus, their application in elastomeric-based composites is very promising. Unfortunately, next to their wonderful properties, there are some disadvantages significantly suppressing their wide utilization in the real-life application. The main disadvantage is their poor dispersibility within the elastomeric materials, due to the high interparticle interactions caused by the phenomenon called  $\pi$ - $\pi$  stacking [8]. Therefore, if the unmodified CNTs are dispersed in the elastomeric matrix the large agglomerates are created and they are acting as a stress concentrators causing lowering of the mechanical and electrical properties [9-11]. In order to improve the dispersibility of the CNTs especially in the elastomeric matrices, CNTs surface modification is very effective way. Due to the proper CNTs dispersion, basic material properties can be improved and CNTs-based composites can be shifted towards various real-life application with enhanced performance [12].

This book chapter briefly introduces various types of modifications usually applied to achieve better dispersibility of CNTs in the elastomeric matrices. These modifications include functionalization with various organic substances and non-covalent or covalent modifications having positive effects on the CNTs dispersibility. This chapter also describes several techniques of the composite preparation such as melt mixing, solution mixing or *in situ* polymerization and their impact on the overall dispersibility. Other complementary techniques (i.e., ultrasonication or ball milling) will be also mentioned. Techniques for proper dispersion evaluation such as electron microscopy investigation, investigation of the rheological properties, AC and DC conductivity evaluation will be briefly described as well.

Modification of the CNTs considerably influences the viscoelastic properties (viscoelastic moduli, loss factor and viscosity) and electrical properties therefore one part of the chapter is devoted to this issue. Viscoelastic moduli and loss factor are crucial parameters, indicating successful or unsuccessful improvement in case of dispersion and those will be investigated more in detail. Electrical properties are usually consistent with the viscoelastic ones and if one of them is improved the later usually confirms this behaviour as complementary method.

The last part of this chapter is focused on the potential application of the CNTs elastomeric composites as very promising photo-actuators. Modifications described in this chapter lead to the improvement of the dispersibility of the CNTs in the elastomeric matrices and significantly influences the mechanical or electrical properties. All these properties are connected to the photo-actuation phenomenon. Proper dispersion of the CNTs in the elastomeric matrices causes effective redistribution of the photo energy within the material and thus reversible contraction (light on) and expansion (light off) can be significantly magnified. Such prepared elastomeric composites consisting of modified CNTs are very promising for application as effective photo-actuators in various technological areas such as artificial muscles or light-driven plastics [13-15].

## II. MODIFICATION OF CARBON NANOTUBES FOR APPLICATION IN ELASTOMERIC MATERIALS

As already mentioned, the conjugated surface of carbon nanotubes does not provide the sufficient interactions with polymer matrix for efficient load transfer. The suitable surface modification can provide solution for both, the

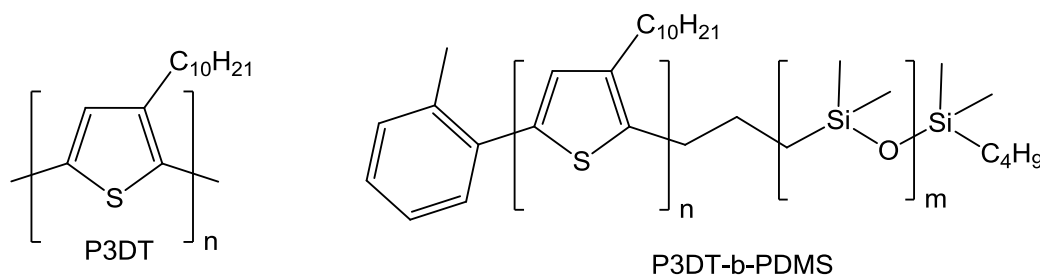
disentanglement as well as improvement of stress transfer to polymer matrix. There are several approaches of surface treatment in term of degree of deterioration of the conjugation on the CNT surface, i.e. the non-covalent and covalent approaches.

#### A. Non-covalent Modification of Carbon Nanotubes

The non-covalent modifications are based on physical interactions between the dispersion agent and the filler surface. The dispersion agents should decrease the surface tension of CNTs, and hence prevent the van der Waals interactions between the tubes and suppress aggregates formation. Various types of surfactants and polymers have been utilized in this issue. The surfactants are low molecular compounds consisting of hydrophobic tail and hydrophilic head [16], further differentiated as non-ionic, anionic, cationic. The efficiency is dependent mainly on the type of surfactant and polymer matrix. The attraction between filler surface and surfactant can be provided by charge or by  $\pi$ - $\pi$  stacking between delocalized electrons of carbon surface and those from aromatic part of the surfactants [17].

The phenyl groups bearing anionic surfactants were recognized as more efficient compared to linear anionic surfactants. The efficiency can be enhanced by increasing number of phenyl groups, the utilization of three phenyl group bearing surfactant resulted in most stable CNT dispersion in natural rubber (NR) latex [18]. Although the surfactants can assure better dispersion in the matrix, the surface modification may lead to hindering the phonon and photon transport that reflects in suppressed thermal and electrical conductivity compared to neat CNT composites [19, 20].

The surface modification of CNT through interaction with polymers has been reported as well. The CNT stabilization with chitosan salt was utilized for dispersion in silicone rubber [21]. The statistical poly(ethylene-*co*-polyvinyl acetate) copolymer was used as CNT compatibilizer in ethylene propylene rubber [22]. The block copolymer wrapping was found to be more advantageous compared to homopolymer in term of electrical percolation threshold in poly(dimethylsiloxane) (PDMS) matrix [23]. The single-walled carbon nanotube (SWCNT) were modified either with poly(3-decylthiophene) (P3DT) homopolymer or poly(3-decylthiophene)-*b*-polydimethylsiloxane (P3DT-*b*-PDMS) block copolymer (Scheme 1) and used as a filler in PDMS matrix. The percolation threshold of 0.05 wt. % and 0.02 wt. % was reported for cases of homo and diblock copolymers, respectively. The decrease of percolation threshold value was ascribed to better dispersion due to PDMS block.



Scheme 1 The structures of homo and block copolymers used for CNT modification [24]

The non-covalent modification is rather simple to perform, the chemical structure of the filler surface is not disrupted and retains its electrical properties [24]. On the other hand, the physical interactions are weak and leading to rather weak stress transfer from polymer matrix to CNTs and the surfactants swell out from the composites upon thermal exposure.

#### B. Pre-treatment of Carbon Nanotubes for Covalent Modification

Carbon nanotubes bundles contain residual impurities from the fabrication process, namely amorphous carbonaceous materials and metallic residues from catalytic system. Both can affect the desired properties; therefore they tend to be removed before CNT utilization. Various methods of CNT purification have been reported [25]. Among them the method based on chemical treatment and thermal annealing, which is the most frequently used. The chemical methods usually employ acids that enable removing the catalyst residues. Simultaneously the functional groups are formed on the surface. The thermal annealing, on the other hand, enables to remove the amorphous carbon as well.

The effect of pretreatment method on composite electrical properties was investigated and it was concluded that thermal pretreated CNT (t-CNT) poses better dispersion and thus lower electrical percolation threshold compared to acidic pretreated CNT (a-CNT) [26]. Unlike the a-CNT, the t-CNT exhibited expectable percolation dependence. The absence of percolation in a-CNT composite was assigned to pure dispersion caused by excess of functional groups on the CNT surface resulting in aggregation into clusters. On the other hand, the thermal annealing enables restoring of the defects in CNT structure.

The annealing temperature can be used to control the hydrophobic/hydrophilic CNT properties. The purification of multi-walled carbon nanotubes (MWCNTs) performed at 2800 °C resulted in restoring the defects in graphitic structure and made the surface hydrophobic, so thus inert to interact with fluorinated NR matrix. On the other hand, the extra hydrophilic

CNTs prepared at 1300 °C provide sufficient interactions with matrix and thus better mechanical performance at elevated temperatures [27]. Similar effect of temperature thermal treatment on dynamic mechanical properties of NR composite was reported also by Takeuchi et al. [28].

The acidic treatment can be used in purification process, as a primary step in multi-step covalent modifications, or sometimes is even designated as functionalization responsible for substantial changes in material performance through strong interactions or even forming covalent bonding with polymer matrix. For example, the nitrile groups of acetonitrile butadiene rubber were reported to provide strong donor-acceptor interactions with hydroxyl and carboxyl groups present on oxidized surface of MWCNT. These interactions led to enhancement of storage and loss modulus, and solvent swelling characteristics of polymer matrix [29]. The effectiveness of acidic modification on CNT dispersion was reported also in less polar elastomers; 4 wt. % COOH groups on MWCNT was responsible for good dispersion in thermoplastic polyurethanes (TPU) and dramatic increase in dielectric constant compared to neat matrix; the comparison of results with neat MWCNT was not discussed [30]. Similar trend was reported in NR composite [31].

Gaharwar et al. reported covalent linkage between acidic treated CNT and poly(glycerol sebacate). The linkage was formed between the carboxyl groups on CNT surface and hydroxyl groups present as side groups on the polymer chains [32].

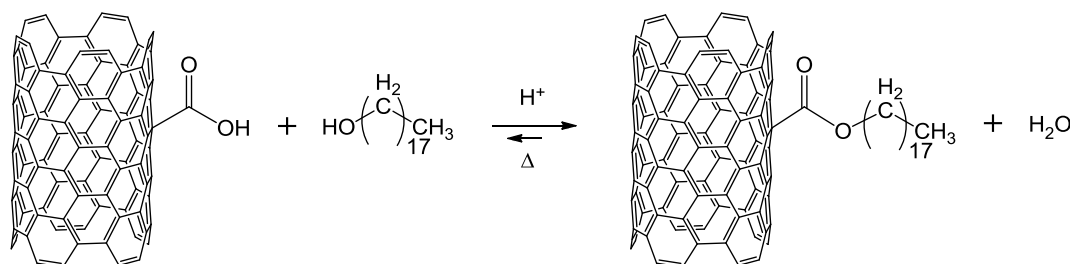
### C. Covalent Modification of Carbon Nanotubes with Low Molecular Weight Substances

The energy of carbon-carbon bond reaches 350 kJ/mol, while the energy of strongest non-covalent bond, hydrogen bond, is approximately 21 kJ/mol. The strength of covalent bonds is one order of magnitude higher than non-covalent interactions. It will ensure effective stress transfer from the matrix.

The modifications of carbon nanotubes with low molecular weight compounds are usually performed in two steps including introduction of functional groups and their post-modifications. The options of primary functionalization of CNT surface have been summarized in excellent reviews [33, 34]. In the praxis, the oxidation and diazotation are the most commonly utilized procedures. The oxidation leads to formation of the functional groups, preferably at the edges or defect sites of the CNT surface [35]. On the other hand, the diazotation provide more uniform sidewall functionalization and can be performed at milder conditions [36].

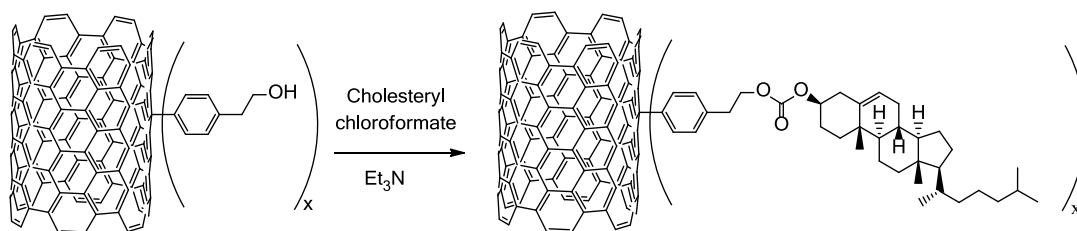
Oxidation introduces hydroxyl, epoxy and carboxyl groups on the CNT surface. The subsequent post-modification can be performed by esterification or amidation of carboxylic groups with alcohol or amines, by reaction hydroxyl or epoxy groups with isocyanates or amines, or silanization of hydroxyl groups [33].

The esterification of oxidized CNT was employed by Thomas et al. [37]. CNTs were first oxidized with 1-octadecanol, as illustrated in Scheme 2. The aliphatic functionality was reported to improve CNT dispersion in NR.



Scheme 2 Synthesis of octadecanoate modified CNT via esterification of carboxylated CNT with 1-octadecanol [37]

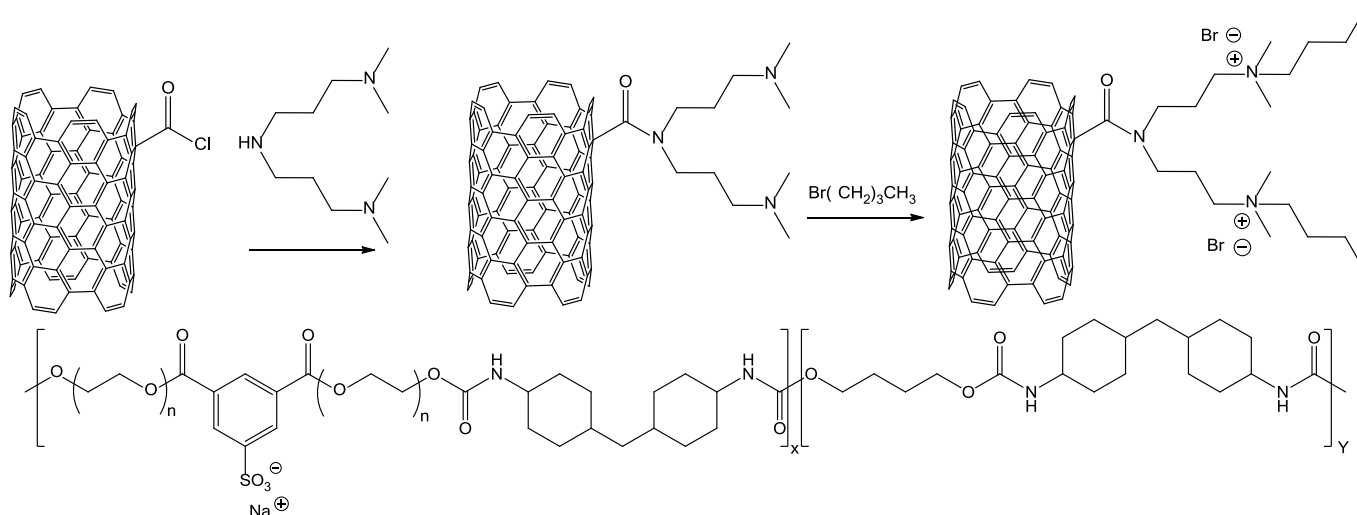
Another simple two-step approach is shown in Scheme 3 [38]. The 4-aminophenethyl alcohol was attached to CNT surface via diazotation. Then the hydroxyl groups were esterified with cholesteryl chloroformate to obtain aliphatic and sterically spacious functionalization. The cholesteryl groups provides improved interactions with aliphatic chains, such as poly(ethylene vinyl acetate) (EVA) [39] or isoprene block in poly(styrene-*b*-isoprene-*b*-styrene) (SIS) [40], as was revealed by dielectric spectroscopy, dynamic mechanical analysis and melt rheology.



Scheme 3 Modification of MWCNT with cholesteryl chloroformate through esterification of 4-(2-hydroxyethyl)phenyl-modified MWCNT [39]

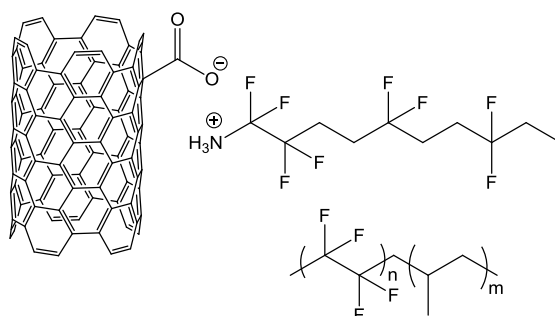
In previous examples, the interactions of the functionalized fillers with polymer matrices were based on simple van der

Waals interactions. Gao et al. [41] presented procedure based on ionic interactions between filler and matrix. They prepared covalently modified CNTs with dendritic ammonium cation that were used as filler for anion-grafted polyurethane matrix. The modification strategy is shown in Scheme 4. The carbonyl chloride grafted CNTs were reacted with secondary amine to introduce tertiary amines onto the CNT surface. They were quaternized with 1-bromobutane to obtain ammonium salt. The electron microscopy observation revealed good dispersion. The modification was expected to provide interactions between the polyurethane hard segment and CNT. However, the effectiveness by direct comparison of composite properties containing neat CNT was not provided.



Scheme 4 Sulfonated polyurethane bearing anion moiety and carbon nanotube modified with dendritic ammonium cation [41]

The combination of both the ionic and van der Waals interactions was presented by Meng et al. [42]. Ionic interactions were utilized for modification of negatively charged carbon nanotubes with cationic fluorocarbon surfactant to obtain good dispersion in fluoroelastomer (see Scheme 5).



Scheme 5 The strategy of dispersion of carboxylated CNT in fluoroelastomer with aid of cationic fluorinated surfactant [42]

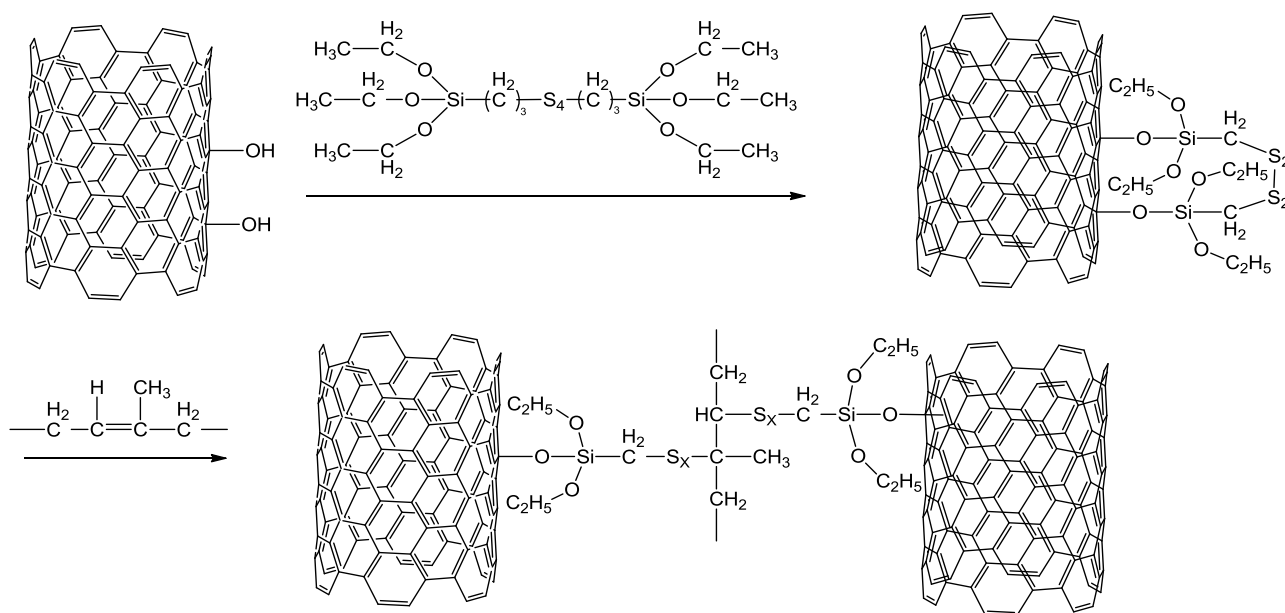
#### D. Covalent Modification of Carbon Nanotubes with Polymer Chains

The grafting with polymer chains ensures high compatibility of the CNT with polymer matrix. The polymer chains bonded on the CNT surface interact with matrix at interface and affect the matrix performance. The affected part is called interphase and exhibits different properties compared to bulk neat polymer. The polymer grafting enables to vary thickness of the polymer layer, structure, density and thus the interface ratio effectively. Among these parameters, the polymer grafting density,  $\sigma$ , provides the most useful information considering the polymer chain arrangement on the surface. It affects directly the surface properties of the filler such as interfacial localization of terminal groups, steric repulsive forces, diffusion control, wetting and many other parameters [43]. The rarely anchored polymer chains are present in “mushroom” regime, while the densely attached chains are present in “true brush” regime. The mushroom-to-brush transition was observed at around  $\sigma \sim 0.065$  chains/nm<sup>2</sup> at surface grafted with poly(acrylamide) [44]. The grafting density can be controlled namely by the choice of the grafting method. There are two approaches of polymer grafting, namely “grafting to” and “grafting from” approach.

The “grafting to” methods involve the attachment of the polymer chains to reactive sites present on the CNT surface. This approach provides rather low grafting density, due to steric hindrance already attached on polymer chains that prevents diffusion of other polymer chains toward the free reactive sites on CNT surface. Only polymer chains containing reactive functional groups can be used in this technique. Among the “grafting to” techniques also attachment of the polymers to CNT during composite processing, such as ultrasonication or melt mixing, can be included. For instance, Li et al. [45]

utilized reaction between maleic anhydride and amine for grafting polypropylene (PP) onto MWCNT. The amine functionalized MWCNTs were first melt-blended with maleic anhydride grafted PP chains at 220 °C, and subsequently the grafted MWCNTs were melt-blended into ethylene propylene diene terpolymer (EPDM) matrix. The authors observed increase of elastic modulus and toughness. However, the authors did not provide protocol of purification of the grafted MWCNT from the free polymer chains. Thus, it can be supposed that the mixture of PP and grafted MWCNT was used as filler. From this point of view, the approach does not pose sufficient control over the process and the final material composition.

Another approach is to introduce functionality providing opportunity for formation of covalent bonding during vulcanization process of rubber. The double bond in isoprene unit of NR was employed for covalent attachment of carbon nanotubes modified with bis(3-triethoxysilylpropyl) tetrasulfide [46]. The grafting was conducted during composite preparation process. The scheme of composite preparation is shown in Scheme 6.

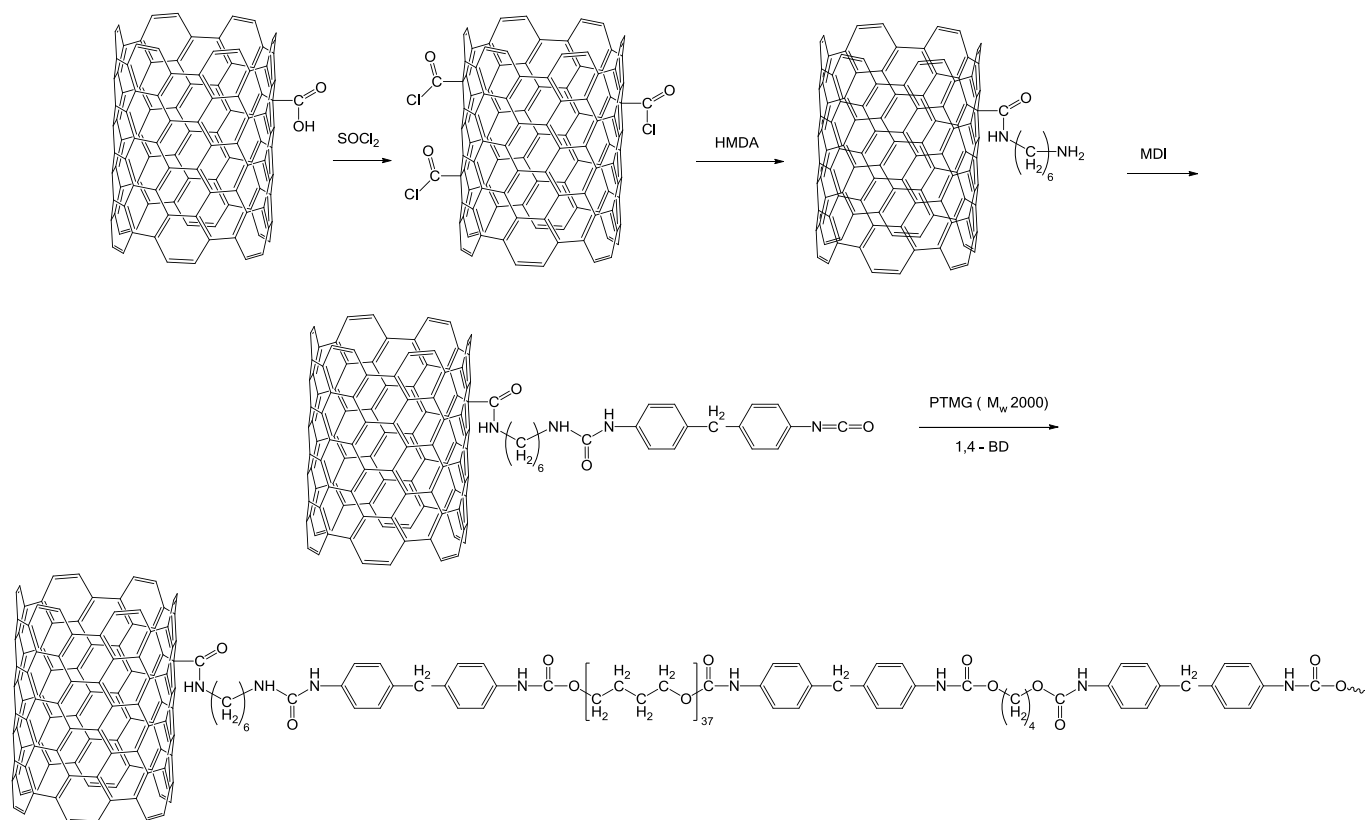


Scheme 6 (a) Introduction of Sulphur atoms on CNT surface by silanization; (b) covalent grafting of CNT to NR [46]

Silanization of carboxylated CNT was used to introduce amine functionality onto CNT surface to provide covalent bonding with epoxidized NR [47].

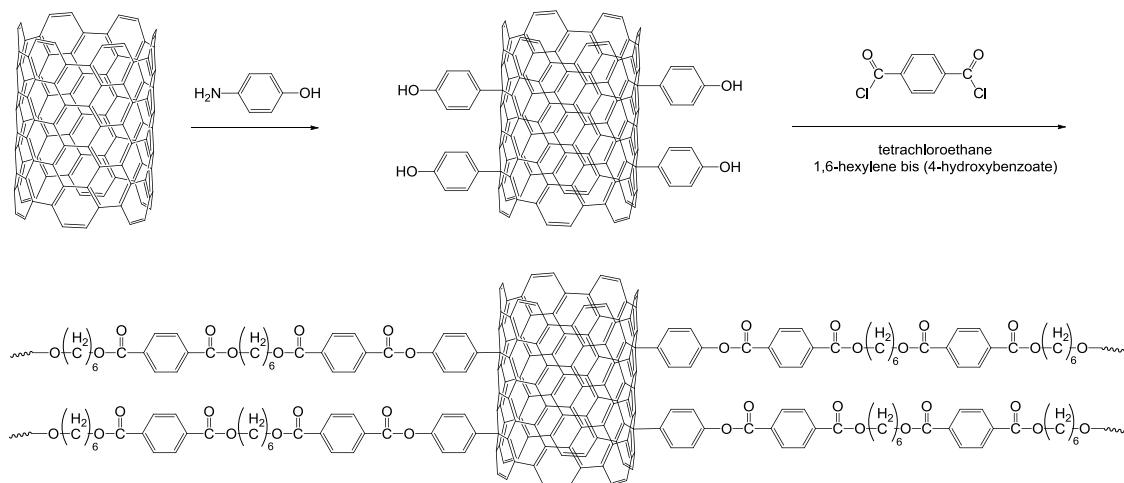
“Grafting from” approach is based on polymer growth from the initiators bounded on the CNT surface. In this way, all the polymer chains grow simultaneously and thus polymer chains with high degree of polymerization densely packed on the surface can be obtained [48]. The detailed description of grafting techniques can be found in many review articles [34, 35, 48]. The polycondensation, ionic, as well as radical polymerization techniques have been employed for grafting of polymers from CNT surface in order to obtain elastomer composites with good CNTs dispersion.

Im et al. [49] grafted thermoplastic polyurethane elastomer (TPU) from MWCNT surface according to Scheme 7. The grafting density was not estimated. The composites containing 0.5 wt. % of both grafted and neat MWCNT were prepared by melt mixing in twin screw extruder. Compared to neat matrix both types of composite exhibited higher storage modulus below  $T_g$  as revealed by dynamic mechanical analysis. The highest modulus was observed for composite containing grafted CNT. Tan delta temperature dependence showed shift in  $T_g$  from -21.7 °C for neat matrix and composite with neat CNT to -17.5 °C for composite containing grafted MWCNT.



Scheme 7 Modification of carbon nanotubes with polyurethane [49]

The polycondensation was employed also by Wu et al. [50], who grafted CNT with liquid crystals. They performed polycondensation of 1,6-hexylene bis(4-hydroxybenzoates) and terephthaloyl chloride on the hydroxyphenyl-functionalized CNT surface as shown in Scheme 8. The amount of grafted polymer was determined by TGA was 56 wt. %; the density of grafting was not evaluated. The modified CNTs were dispersed in thermotropic liquid crystalline polymer (TLCP) solution by using ultrasonication. Solvent evaporation resulted in composite formation. DSC results revealed that addition of 3 wt. % of grafted nanotubes provided enhancement of anisotropy-to isotropy transition temperature of TLCP matrix by 18 °C. The enhancement is assigned to both good dispersion of CNT and strong interactions between aromatic CNT surface and mesogenic groups of polymer matrix interacting through  $\pi$ - $\pi$  attraction. Unfortunately the comparison to neat CNT was not reported.



Scheme 8 Modification of carbon nanotubes with liquid crystals [50]

Gerate et al. [51] grafted polystyrene from MWCNT surface using surface-initiated atom transfer radical polymerization (SI-ATRP). The  $M_n$  was 9200 g/mol, the amount of PS was determined by TGA to be 10.2 wt.%, and number of polymer chains on one nanotube was estimated to be in average of  $5.2 \times 10^3$ . Based on AFM images, the authors claim that such modification do not pose satisfying dispersion in SIS matrix without aid of dodecanethiol surfactant. Contrary to findings state above, the CNT grafted with PS (3900 g/mol and 48 % wt. %, grafting density 0.5 chains/nm<sup>2</sup>) showed improved

dispersion and increased elasticity of SIS compared to neat CNT as revealed by microscopy, DMA and rheological investigations [35].

The difference in CNT performance is probably caused by various grafting densities of the PS chains. Although the molar mass of PS in reference [52] reached only 3900 g/mol, the grafting density calculated with respect to CNT surface area was 0.5 chains/nm<sup>2</sup>. Unfortunately Gerate et al. [51] did not mention surface area of CNT, however it can be found in reference [53], that the grafting density of PS chains is approximately 0.03 chains/nm<sup>2</sup>. This one order of magnitude lower chain density could be responsible for the insufficient dispersion observed by Gerate due to different arrangement of grafted chains.

The most effective approaches for reinforcement of elastomeric composites are based on *in-situ* polymerizations. The monomers are polymerized in the presence of filler that can be effectively dispersed. Several variations of *in-situ* composite preparations were reported. Either the monomers were used only for synthesis of a polymer matrix in the presence of neat or already modified particles, or the monomers were grafted from particles to form composite with only grafted polymer chains, or the monomers were both grafted from the particles to form grafted particles and simultaneously grown from sacrificial initiator to form also the polymer matrix [40].

It is worth to note that the final composite performance with respect to effectiveness of the CNT surface treatment is strongly affected by composite preparation method. In case of vulcanized rubbers, it was reported that the presence of CNT and nature of their modifications affected the curing process in both favorable [54] as well as adverse way, resulting in less dense cross-linking that affected the composite properties in term of enhanced plasticity, decreased modulus and  $T_g$  [55, 56].

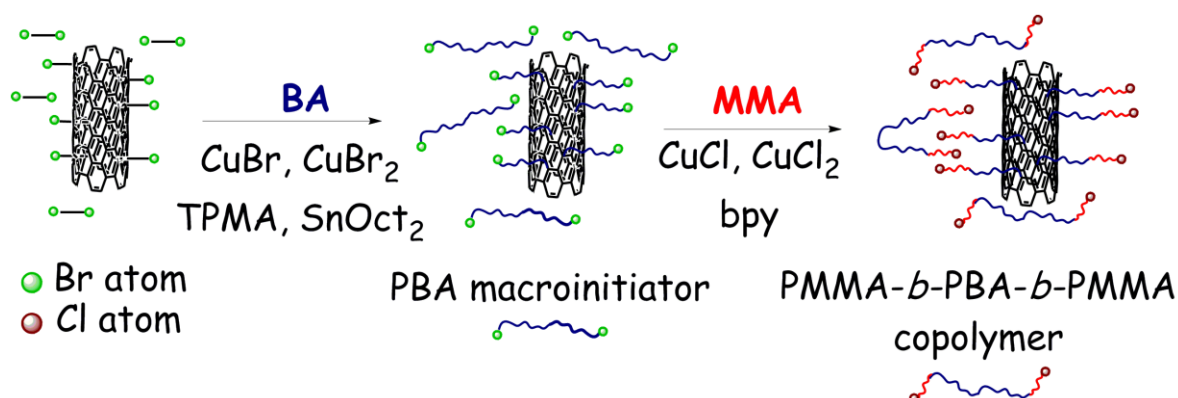
De Falco et al. [56] prepared SBR composite containing CNT grafted with poly-4-vinylpyridine (PVP). The modified CNTs were added to toluene solution of SBR and vulcanization reagents. Then the film was formed after solvent evaporation and melt-blending operation, and vulcanized at 150 °C. The enhanced plasticity and decrease of  $T_g$  was observed with increasing filler content. The authors excluded the possibility of the effect of interaction of the PVP with vulcanization reagent Zn, although it is well known, and the effect was ascribed to changes in cross-linking type or density without further investigation. The effect of neat CNT was not shown for comparison.

Similarly the decrease of mechanical performance was reported by Galantini et al. [55] who prepared PUR composite in presence of CNT modified by *in-situ* polycondensation. They grafted CNT with either acrylonitrile or diurethane acrylate under RAFT conditions. Then CNTs were dispersed in CHCl<sub>3</sub> and placed into reaction mixture of polyol and diisocyanate to produce composite. Both modifications resulted in decrease of elastic moduli compared to neat matrix as well as composites containing neat CNTs. The effect was pronounced in diurethane acrylate modification and was ascribed to inhibition of curing process in matrix due to fine dispersion and good interactions with matrix component. While the dielectric constant increased rapidly after addition of neat CNT, the modification suppressed the dielectric response of CNT, however still values were slightly higher than for neat matrix. Simultaneously diurethane acrylate modification was reported to provide highest electromechanical response at 0.5 wt. % filler loading.

Similar obstacles were reported for ionic polymerization of polyisoprene. The isoprene was polymerized in the presence of sacrificial initiator and SWCNT bearing carbanion initiator. The monomer conversion in such system reached 62 % while in absence of CNT 90 %. The difference was caused by side reaction promoted in the presence of filler. Nevertheless, the final composite containing 1 wt.% of SWCNT exhibited increase in  $T_g$  of PI by 14 °C [57].

The improvement of mechanical performance was reported in some systems based on polymer chains grafted from CNT surface in absence of sacrificial initiator, i.e. free polymer chains in final composite. Jiang [58] grafted poly(butyl acrylate)-*co*-poly(methyl methacrylate) (PBA-*co*-PMMA) copolymer onto the CNT surface using SI-ATRP under Activators ReGenerated by Electron Transfer conditions (ARGET SI-ATRP). This strategy enables to control the copolymer polydispersity index (PDI). The co-monomer ratio affects the mechanical performance of the resulting composites. In this approach, the polymer chains are covalently bond to CNTs that provide efficient restriction of chain motion and thus act as additional cross-linking points in thermoplastic elastomer TPE system. As could be expected both MMA and CNT content affected the mechanical properties in term of increase of modulus, strength and better strain-recovery.

The state of the art strategy with respect to grafting, filler content, matrix morphology pose the approaches based on grafting block copolymers by surface initiated controlled polymerizations. Such block copolymers can exhibit properties of thermoplastic elastomers. Recently the preparation of linear triblock copolymer under ARGET ATRP conditions, and simultaneous grafting CNT with diblock copolymer to obtain composite PMMA-*b*-PBA-*b*-PMMA containing CNT-*g*-PBA-*b*-PMMA is shown in Scheme 9 [59]. The synthesis strategy enabled full control over the polymer morphology, as well as preferential interactions of CNT with soft PBA block.



Scheme 9 The synthesis strategy of preparation CNT-g-PBA-*b*-PMMA/PMMA-*b*-PBA-*b*-PMMA nanocomposite using ARGET ATRP [59]

Compared to neat triblock copolymer matrix the composite containing modified CNTs increased selectively  $T_g$  of the PBA phase by 5 °C, since the CNT were preferentially interacted/or even located in the soft elastomeric phase. For comparison in the case of composites containing CNT grafted with PBA homopolymer or neat CNT, the  $T_g$  was increased by 3 °C or only negligibly, respectively [40]. The overall elasticity of these three composite types was found to be highest in the case of diblock copolymer grafted CNTs.

### III. PREPARATION OF CARBON NANOTUBE-BASED ELASTOMERIC COMPOSITES

This section of the chapter is focused on the preparation techniques used for CNT-elastomer composite fabrication. As it was already mentioned in the case of elastomer-based composites, CNTs are present mostly in form of agglomerates. In order to ensure good dispersion of the CNTs in elastomeric matrix, various modifications were described in previous section and provide suitable route to obtain materials with proper mechanical, electric or photo-actuating properties.

#### A. Effect of Modifications on the Dispersibility of Carbon Nanotubes

Dispersibility of the fillers in the elastomeric matrices is crucial parameter influencing the overall properties of the final product and approach how properly is filler introduced to the elastomeric matrix and which technique is utilized finally lead in variety of the physical properties influencing their further application.

All techniques for CNT modification (i.e. non-covalent [60, 61], covalent modifications with low molecular substances [17] or covalent modifications with short polymer chains) lead to improvement of the CNTs dispersibility in elastomeric matrices [62, 63]. The crucial point for successful dispersion is modification of the CNTs with substances of chemical similarity to the elastomeric matrix (Fig. 1). Otherwise, CNTs will create individual islands of clusters or agglomerates due to the  $\pi$ - $\pi$  stacking or will be phase separated due to incompatibility of the grafted polymer layer with the elastomeric matrix (Fig. 1 left). On the other hand, in those CNTs which are modified with substances similar to elastomeric matrix, strong  $\pi$ - $\pi$  stacking can be interrupted, due to increased interparticle distance and better compatibility with the elastomeric matrix (Fig. 1 right) allowing sufficient space between CNTs for elastomeric chain penetration and thus improved dispersibility of them within the matrix that can be achieved.



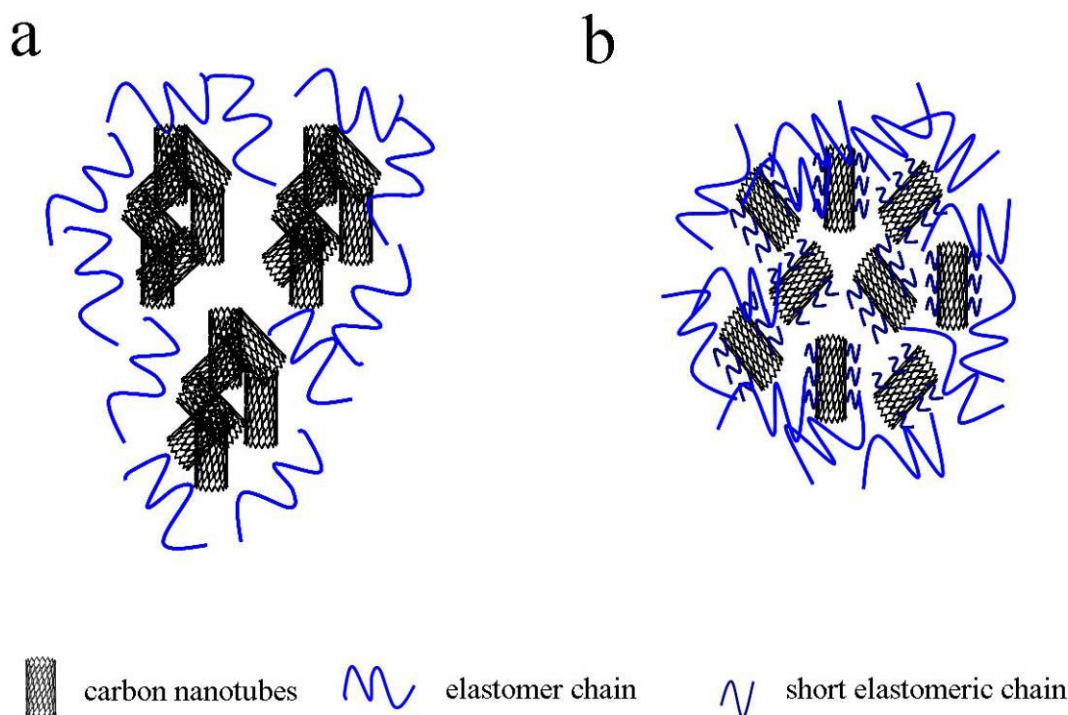


Fig. 1 Schematic illustration of the composite formation after mixing of the CNTs into the elastomeric matrix, (a) unmodified CNTs and (b) modified CNTs with short polymer chains

## B. Mixing Techniques

### 1) Melt Mixing

The first technique for sufficient dispersion of the filler into the elastomeric matrices is melt mixing. Since elastomeric matrices can be divided into two big groups, thermoplastic elastomers (TPEs) and those based on curable polymers, therefore also the melt mixing techniques have to be performed accordingly.

For CNT elastomeric composites based on TPEs mixing with extruder which is frequently used for masterbatch preparation (elastomeric material with filler and other components in form of granules or pellets) is very commonly applied (Fig. 2) [64]. TPEs have main advantage from the processing point of view. These elastomers have physical cross-linking which can be repeatedly processed (similarly as thermoplastics) and CNT-based filler can be added at various stages of TPE processing [20, 65]. Kumar et al., also proved that modified CNTs can be effectively processed using extrusion technique without any impact on this modification. Moreover, such prepared composites had enhanced thermal and electric properties due to the improved interface properties between matrix and surface-modified CNTs [66].

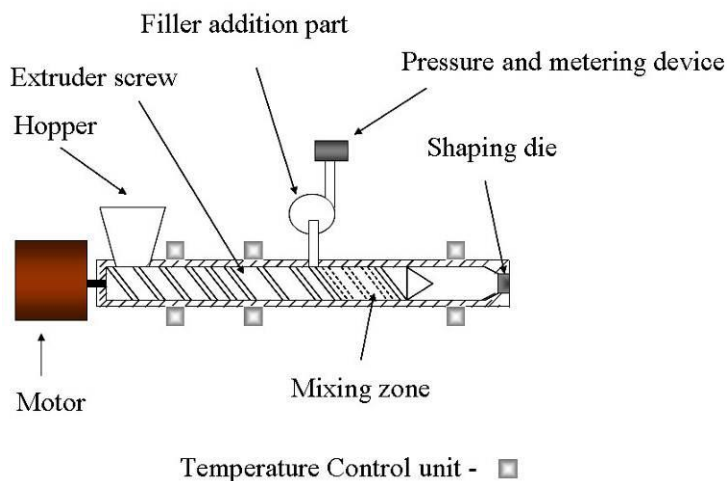


Fig. 2 Schematic illustration of the extruder used for processing of elastomeric materials with various fillers [64]

Unfortunately, for the second type of CNT elastomeric materials based on curable polymers, there is a disadvantage from the processing point of view. This material is consisting mainly of the filler, elastomer and curing system. As can be seen in the Fig. 3, within the mixing at certain temperature this compound has only limited processing window. After certain period of time, compound starts to be chemically cross-linked which causes irreversible structure formation. Moreover, when the 90 % of the maximum torque is achieved, materials are cured and have to be removed from processing tool, due to possible negative post-cured behaviour (marching or reversion) [67]. For this kind of elastomeric materials the extruder machine can be effectively used, however only for the limited period of time. On the other hand, suitable modification of CNTs leads to better dispersion and thus shorter mixing times, which is highly desirable for this type of compounding. Moreover, it was proved that modified CNTs with various moieties (hydroxyl or carboxyl) decrease the curing rate and therefore prolong the processing window for modified CNT mixed into the hydrogenated nitrile elastomer [68]. It indicates that proper selection of the CNTs modified allows controlling the range of the processing window for curable polymers.

Another technique for filler mixing into the elastomer matrix is the use of two-roll mill (Fig. 4). This device can be also used in cases that one some components of the elastomeric compound are liquid. The main principle of this device is utilization of the shear forces to the material in the mixing gap, due to the various velocities of the roll mills. Moreover, in some cases, direction of the roll mills rotation can be varied and final configuration mostly depends on the required mixing efficiency. The suitable mixing efficiency and applicability for the compounds consisting of the curing system is adjustable gap between the roll mills (nip) and short residence time of the material in the device [67].

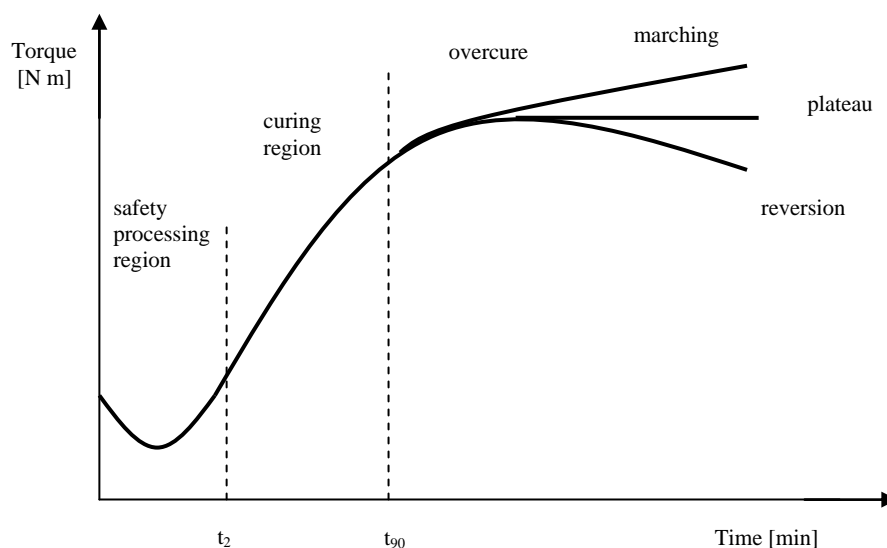


Fig. 3 Curing curve for determination of the safety processing window for chemically cross-linked elastomeric materials [67]

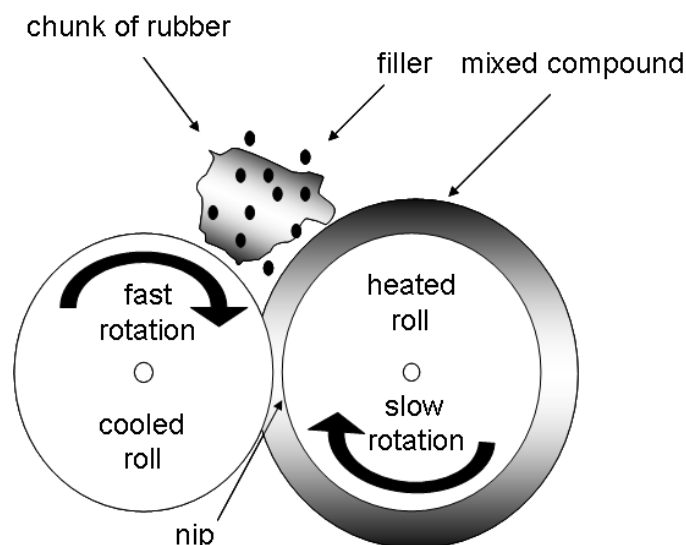


Fig. 4 Schematic illustration for two-roll mill mixing and material going through the nip [67]

After melt mixing, further processing techniques are usually employed in order to obtain final specimen for analysis, and/or final products with required shapes. One of the subsequently applied techniques is compression moulding (Fig. 5). Compounded material including CNTs and elastomeric matrix in the form of pellets or granules is placed into the hot mould usually set to temperature above  $T_g$  and by using of the high pressure the shape of the material is given. There are two possibilities on how to fix the shape of the composite material and they depend on its nature. If the material includes physical cross-linking, final shape of the composite material is achieved by cooling down to temperature below  $T_g$  in order to fix the polymer chains motion. Advantage of TPEs utilization is reversible changing of the composite shape according to the application requirements. In case that elastomeric material is based on chemical cross-linking, the mould is stabilized on the certain temperature and time of compression is based on curing curve conditions (see Fig. 3). After time  $t_{90}$  the composite material is cured, chemical cross-linking is fully achieved and composite shape is irreversibly fixed. Fabricated composite material with final shape can be removed from the mould. Since the curing rate is significantly influenced by modification of CNTs, this technique can be effectively applied once the curing rate can be tailored [69].

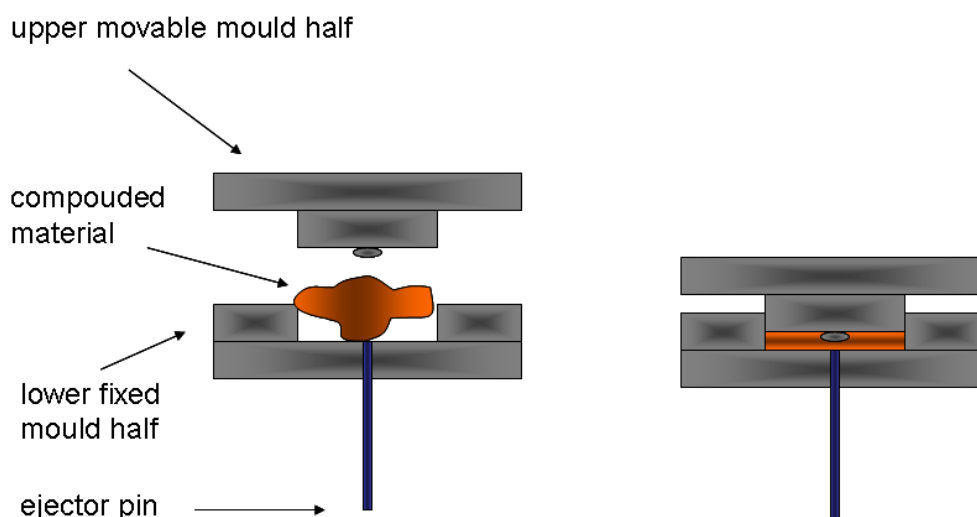


Fig. 5 Schematic illustration of the compression moulding technique [69]

Another approach of the composite material shape fixing is extrusion directly from the extruder through the extruder dies, of various shapes (Fig. 6). Leaving the die, composite material is of requested shape and final shape stabilization is the same as in the case of compression moulding (curing for chemically cross-linked materials and cooling for physical cross-linked materials). This type of composite shape fixing is usually applied for materials with 2D but mainly 3D shape. Generally, the main application is intended for sealing (windows, refrigerators or doors). Nevertheless, this technique is very important from the large-scale fabrication point of view. Modified CNTs mixed into the elastomeric materials as a potential photo-sensors or photo-actuators can be also processed by this approach and indicate that materials described in this chapter are able to be fabricated in industrial scale.

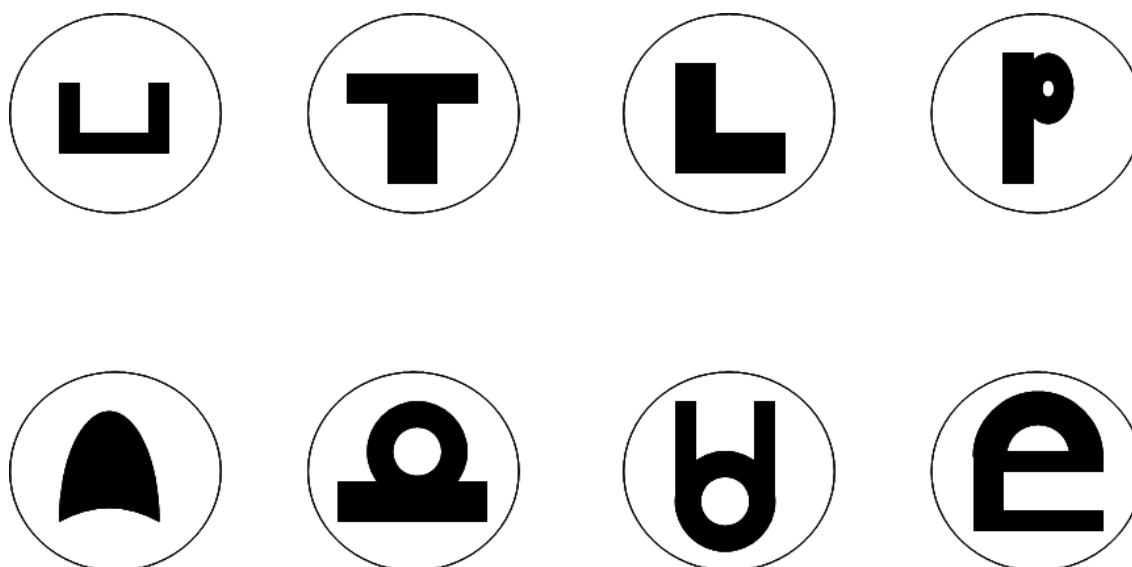


Fig. 6 Schematic illustrations of the extruder die with various shapes of profiles for elastomeric materials processing

The last approach for fixing of the final composite shape is injection moulding. The main aim of this approach is production of 3D products used as sealing for insulation or dumping control [70]. Principle of the injection moulding technique is based on high-pressure composite material transportation from the injection part to the mould, which gives the final shape to the material as shown in Fig. 7. Similarly to the extrusion technique, for both elastomers with physical cross-linking and chemical cross-linking modification of the CNTs causes improved particle dispersion allowing shorter mixing time. Introduction of the modified CNTs influences mainly curable elastomers because the processing window can be tailored and thus possibility of nozzle blockage, due to fast curing is minimized.

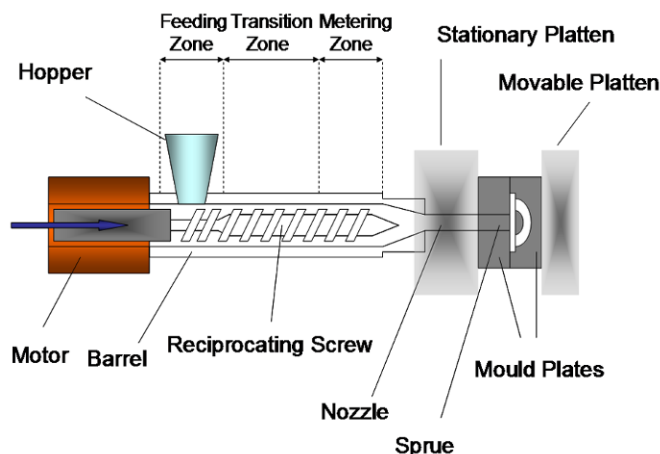


Fig. 7 Schematic illustration of the injection moulding unit for elastomeric composites [70]

## 2) Solution Mixing

Another method for preparation of CNT-based composites is the solution mixing. This procedure is suitable for all thermoplastic elastomers with physical cross-linking having sufficient solvent for proper dissolving. On the other hand, from the group of chemically cross-linked elastomers, for silicone elastomer-based composites, solution mixing is proper procedure. Here is again small disadvantage originates from the processing window which is time limited.

The general procedure for CNT elastomeric composites based on TPEs was used by many authors [70-73] in the following way: CNTs are firstly dispersed mechanically in the solvent and secondly mixed with the help of ultrasonication probe or ball milling [24]. The TPE is dissolved in the same solvent properly. Then the CNTs and TPE are mixed together stirred mechanically with high-speed rotation device [74], or by ultrasonication usually upon application of the probe [17]. Then the solution with proper CNTs dispersion is placed to the mould in order to give the shape to the material and further, at elevated temperature and reduced pressure, the solvent is evaporated. The main advantage of the utilization of modified CNTs are their good interactions with polymer matrix and therefore nearly negligible sedimentation upon solvent evaporation, while composite of neat CNTs exhibits significant sedimentation rate and considerable inhomogeneities can be clearly seen in Fig. 8 [75]. The influence of CNTs dispersion and the compatibility with polymer matrix on the final material properties will be described in detail within the last section.

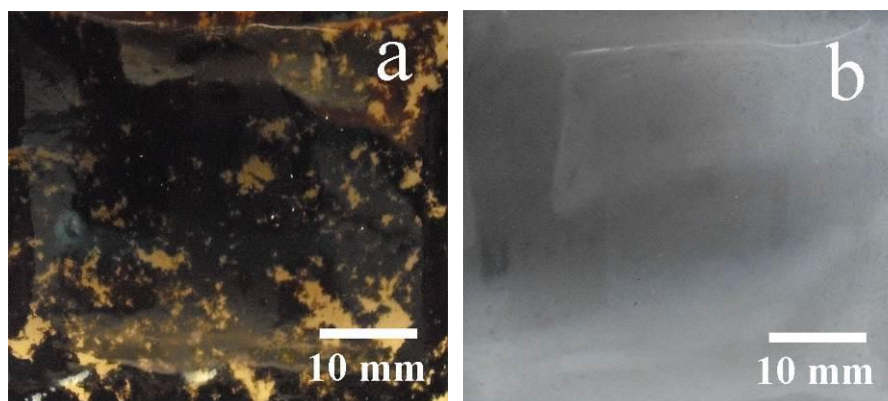


Fig. 8 The composites of SIS: (a) containing 0.12 wt. % of neat CNTs and (b) CNTs modified with short polymer chains [73] (reproduced with permission)

In case of CNT elastomeric composites based on chemical cross-linking polydimethyl siloxane (PDMS), only mechanical stirring is sufficient method since the viscosity of the silicone elastomer is rather high for ultrasonic dispersion and no proper filler dispersion is usually obtained [75]. Therefore the modification of the CNTs in this case is highly desirable in order to achieve proper filler dispersion prior to the final composite cross-linking.

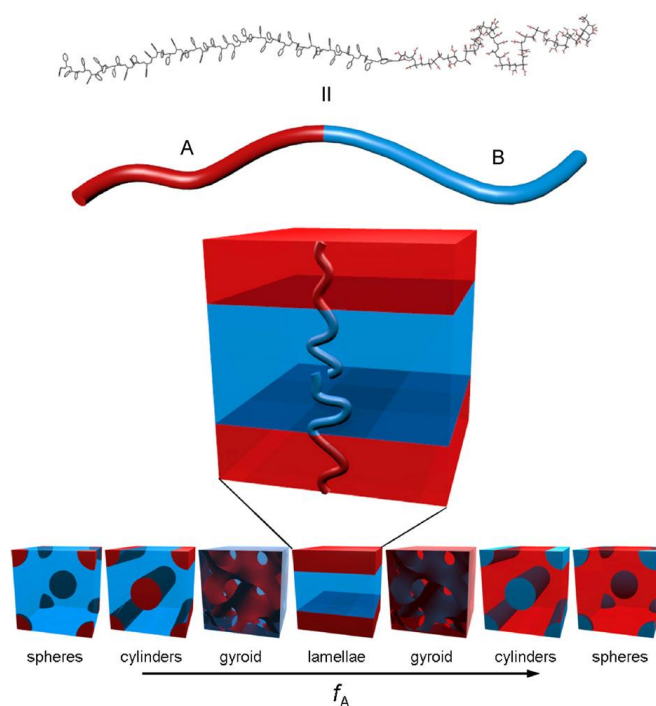
### 3) *In Situ* Polymerization

The last method for effective CNTs dispersion in elastomeric composites is *in situ* polymerization, already mentioned in section II. This approach has been successfully applied by various research groups in order to improve the final composite performance [76-79]. Basically, modified or unmodified CNTs are dispersed in the solution of monomers and solvent and the polymerization often runs under controllable conditions (controlled/living radical polymerizations) this approach enables to provide composite with improved overall properties. In the most cases, the CNTs are covalently functionalized with initiator then mixed with monomer, solvent and sacrificial initiator and polymerization take place. In such mixture, polymer is growing simultaneously and in the same rate from the sacrificial initiator and from initiator attached on the CNT surface. Using controlled/living polymerization techniques enables preparation of macroinitiator, which can be in further step extended by polymerization of another monomer and creates the block copolymers, both in bulk as well as on the CNTs surface. Such approach significantly improves the CNTs dispersibility, due to the increased interparticle distance due to the polymer chains attached on the surface and thanks to good compatibility of the functionalized CNTs properties of final composite materials that can be significantly improved [59].

The last part of this section summarizes the methods applicable for evaluation of the effectivity of CNTs' dispersibility in elastomeric composites. There are several methods of dispersibility evaluation such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images investigation when cross-section of the composite materials are investigated [80]. Furthermore, investigation of viscoelastic properties is crucial method for dispersion evaluation at various temperature regimes (melt rheology in case of physically cross-linked TPEs) [81] or (dynamic mechanical analysis for all elastomeric materials including chemically cross-linked ones) [82]. Another method is based on investigation of the AC/DC conductivity ratio of the CNTs based composites. The great advantage of this method is its non-destructive character [83]. Finally, it can be stated that none of these methods is absolute and for proper investigation and evaluation of dispersibility they must be applied together and further comparison of their results can provide the final assessment.

## IV. EFFECT OF MODIFICATIONS ON THE STRUCTURAL PROPERTIES

The morphology is crucial in term of mechanical performance of block copolymer based thermoplastic elastomers. The hard phase acts as physical cross-linking while soft phase provides the elastomeric performance. Several types of morphologies can be recognized in dependence on the blocks ratio, compatibility of the blocks (expressed by interaction parameter of the monomers) and degree of polymerization. The structures of spheres, cylinders, gyroid or lamellae can be created, as illustrated in Scheme 10 [84]. The carefully chosen CNTs with respect to type and dimensions of copolymer morphology can be located in the domains and thus tune the nanocomposite performance through specific location of CNTs [85].



Scheme 10 Thermodynamically stable diblock copolymer phases [87] (reproduced with permission)

The A–B diblock copolymer, such as the PS-*b*-PMMA molecule represented at the top of scheme 10, is depicted as a simple two-colour chain for simplicity. The chains self-organize such that contact between the immiscible blocks is minimized, with the structure determined primarily by the relative lengths of the two polymer blocks ( $f_A$ ) [84].



The sequestering of CNTs within one phase was for the first time published by Park et al. [86]. They aligned CNTs modified by *in situ* emulsion polymerization of styrene. Authors showed the alignment of PS modified nanotubes into PS phase of lamellar forming polystyrene-*b*-polyisoprene diblock copolymer with molar mass 840 kg/mol and lamellar domain size of 150 nm. Similarly, Liu et al. [46] showed that PS-functionalized CNTs with low surface chain density could be accommodated in the PS phase of poly(styrene-*b*-butadiene-*b*-styrene) (SBS, 30 % PS) regardless of the molar mass of the PS chains, even when  $M_n$  was 330000 g/mol (PDI = 3.10), much higher than that of the PS block of SBS ( $M_w$ =117 000 g/mol, PDI=1.40).

The location of modified CNTs was found to be determined with both molar mass and polymer content. SAXS and TEM results showed that high molar mass (20 kg/mol) and high grafted polymer content (> 90 wt%) of the PS grafted MWCNTs were observed to template the formation of lamellar structure of star polystyrene-*b*-polybutadiene block copolymer with PB core. Contrary to that neat MWCNTs were found to intersect the lamellas [87].

It was also observed that modification of CNT can either prevent the formation of ordered structures or initiate switching to another ordered structure. The cylindrical structure of PS in styrene-*b*-isoprene-*b*-styrene SIS (30 % PS,  $M_n$  58000 g/mol) was lost after incorporation of octadecylamine-functionalized SWCNT. The AFM and FE-SEM images revealed that the addition of surfactant dodecanethiol resulted in formation of composite with ordered lamellar structures with CNTs confined in PS phase. The effect was caused due to enhanced affinity of dodecanethiol modified CNTs and PS phase leading to increased volume of the PS phase [88].

The domain formation is crucial in term of mechanical performance. The neat CNT were found to prevent formation of PS domains of SIS copolymer, resulting in loss of physical cross-linking. The DMA proved that grafting of CNT with PS chains retained the properties of the neat SIS matrix [51]. Another solution was found in modification of CNT with compound compatible with polyisoprene phase, thus preventing interactions with PS phase [38].

## V. EFFECT OF MODIFICATIONS ON VISCOELASTIC AND ELECTRICAL PROPERTIES

As was already mentioned in the previous sections, investigation of the viscoelastic properties is crucial parameter for evaluation of the dispersibility of the CNTs and overall mechanical properties of the CNT-based elastomeric composites. Generally, viscoelastic properties provide information about materials behaviour upon harmonic oscillation [89]. This stimulation can be performed at various regimes. First method is the rheological investigation at elevated temperature when composite material is in the form of polymer melt and usually stimulated by shear forces at various frequencies [90]. Second, is the method of dynamic mechanical analysis utilizing investigation upon wide temperature and frequency range and in this case application of the shear, tensile and compression forces is possible. The basic quantities those are mainly calculated and further investigated are viscoelastic moduli and loss factor. Storage modulus,  $G'$ , reflects the part of the energy which can be stored within material upon dynamic mechanical stimulation. Whereas, viscous modulus,  $G''$ , reflects the part of the energy which is irreversibly changed to heat dissipation within the material upon the same mechanical stimulation. Loss factor (i.e.  $\tan\delta$ ) reflecting the whole material viscoelasticity: lower the  $\tan\delta$  value, better the elastic response of the material on the dynamic mechanical stimulation [38, 40, 56].

In order to successfully evaluate the effect of CNTs modification on the viscoelastic properties, Ilcikova et al. prepared various types of composite materials by solution casting method, when neat CNTs, modified CNT with short polymer chains were prepared [38, 40]. It was clearly observed that, modification of the CNTs caused better dispersibility of the CNTs in the elastomeric matrix and provided sample with significantly improved elastic performance, as shown in Fig. 9.

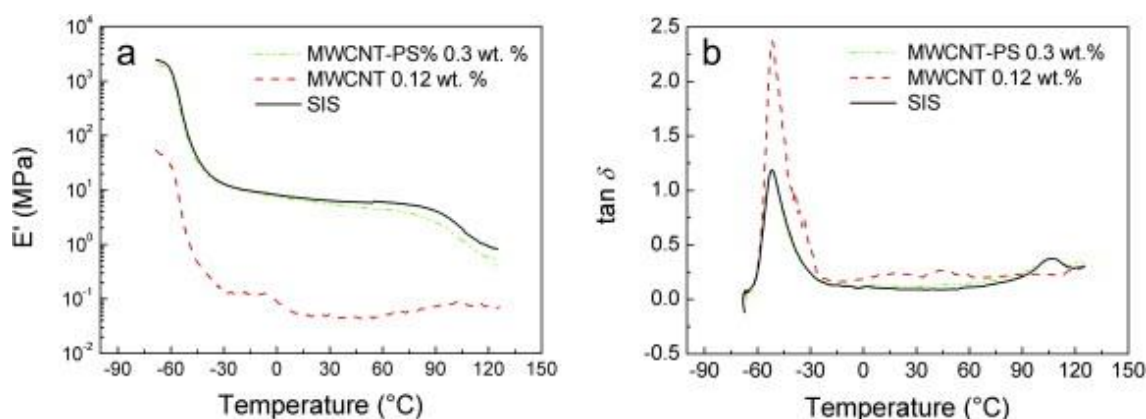


Fig. 9 Viscoelastic properties of modified CNTs with short PS-chains prepared by solution mixing [75] (reproduced with permission)

Same group of authors also focused their research on the possibility of the *in situ* prepared modified CNTs with short polymer chains and in the same time to obtain composite material based on TPEs of the same nature. This approach was recognized as very successful from dispersibility point of view as was already mentioned in the previous part of this chapter,

and further considerably improved the viscoelastic response of the composite materials on dynamic stimulation Fig. 10.

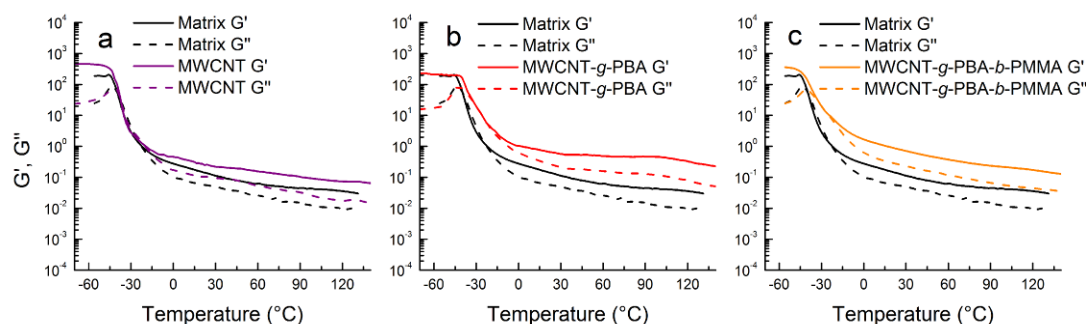


Fig. 10 Viscoelastic properties of variously modified CNTs dispersed in elastomeric matrix via in situ polymerization [40] (reproduced with permission)

Finally, Pedroni et al, performed study dealing with comparison of composite materials containing modified CNTs prepared by solution casting and melt mixing and the effect of preparation method on viscoelastic properties [85]. In this case the melt mixing provided composite materials with improved viscoelastic properties in comparison to the solution casting method. The results were explained by the formation of different morphologies for the elastomeric composite, when shorter time of shape fixing during cooling induced better mechanical response.

Very important property of the CNT-based elastomeric composites is their electrical conductivity. Many authors have been searching the way how to improve the electrical performance of the CNT-based composites [91-93]. Generally, it was stated that excellent electrical properties can be achieved by proper CNTs distribution within the elastomeric composite. Therefore, modification plays an important role [94], however two main theories are presented in the literature. The first theory is based on the proper dispersion of CNTs in the elastomeric matrix leading to the improvement of the electrical properties [95] following by traditional theories for thermoplastic elastomers [35, 96]. The second theory proposed by Terentjev et al. [97] asserts that good dispersion of the CNTs in the elastomeric matrix, in this case PDMS sample, provided material with relatively large distance between individual CNTs and thus electrical conductivity can be lower in two orders of magnitude in comparison to those in which CNTs are in the form of clusters. In clusters, CNTs are in direct contact or only small distances are present between isolated clusters and thus hopping charge transport can be significant. This theory was also supported by Kobashi et al. [98], when agglomerates of CNTs or its dendritic network still in form of clusters provide the rubber composites with 10-fold increase of electrical conductivity.

## VI. EFFECT OF MODIFICATION ON THE PHOTO-ACTUATING PERFORMANCE

The following section of this chapter is focused on the photo-actuation phenomenon and the influence of the CNTs modification on the final photo-actuation performance. Briefly, the photo-actuation phenomenon is reversible change of the material dimensions upon light stimulation. In this case, the utilized material is usually in the form of composite based on elastomers and filler which can redistribute certain amount of absorbed energy within the sample. Upon irradiation (light on) of pre-stretched elastomeric sample the contraction of the polymer chains appears. Extent of the sample contraction usually depends on the irradiation period and light intensity. After removing the light source (light off) sample returns to its initial shape within certain period of time (Fig. 11) [40].

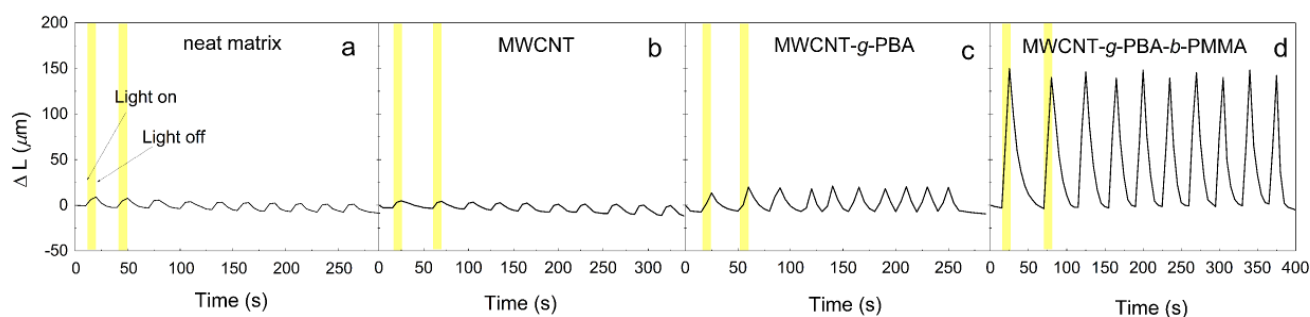


Fig. 11 Photo-actuation performance of CNTs dispersed in elastomeric matrix via in situ polymerization [40] (reproduced with permission)

As proposed by Terentjev et al. [99], proper dispersion of the CNTs in the elastomeric matrix is crucial for the improvement of the photo-actuation performance, since heat redistribution of the energy received from the light in the case of CNTs clusters or agglomerates is rather ineffective. Therefore, huge effort has been spent for non-covalent or covalent

modifications in order to improve dispersibility of the CNTs in the elastomeric matrices.

It was proved that carbon-based filler after successful modification provided composite materials with improved filler dispersibility and thus enhanced photo-actuation performance [100]. Moreover Feng et al. claimed that CNTs modified with graphene sheets as a hybrid filler in the polyurethane elastomeric (PU) matrix, significantly improved the photo-actuation performance, due to strong interactions between the nanofiller and PU matrix resulting in enhanced thermal conductivity leading to better heat distribution within the sample [101].

Czanikova et al. utilized the cholesteryl 1-pyrenecarboxylate (PyChol) as low molecular weight substance for non-covalent modification of the CNTs [102]. PyChol, due to the strong  $\pi$ - $\pi$  stacking phenomenon, intensively interacts with CNTs surface and further improves their dispersibility in the EVA elastomer. This was confirmed by SEM investigation of the cross-section of the CNT-PyChol-based EVA composites. Moreover, since the dispersion was significantly improved also photo-actuation performance was considerably enhanced.

Covalent modification of the samples by low molecular weight substance cholesteryl chloroformate as well as short polystyrene chains was performed on the surface of the CNTs for dispersion improvement in the styrene-*b*-isoprene-*b*-styrene (SIS) elastomeric matrix. These modifications were deeply described in section II of this chapter. Enhanced dispersion was observed in the composites prepared by solution casting for both types of composites the modification resulted in the enhanced photo-actuation performance, as shown in Fig. 12 [38]. As can be seen from Fig. 12 composites containing neat CNTs provide quite good photo-actuation performance for 0.15 wt. % of filler, but the base line of this material and thus mechanical properties upon irradiation is rather unstable due to the poor compatibility with SIS matrix. Furthermore, after covalent modification with cholesteryl chloroformate (Chol), substance preferentially interacts with isoprene polymer, the baseline stabilization was improved and composite material containing 3 wt.% of modified CNTs with Chol is able to actuate. Finally, if the CNTs were modified with short PS chains, the most stable photo-actuating properties were observed, due to the improved compatibility with PS polymer, significantly stabilizing the baseline and thus mechanical response to the light stimulus.

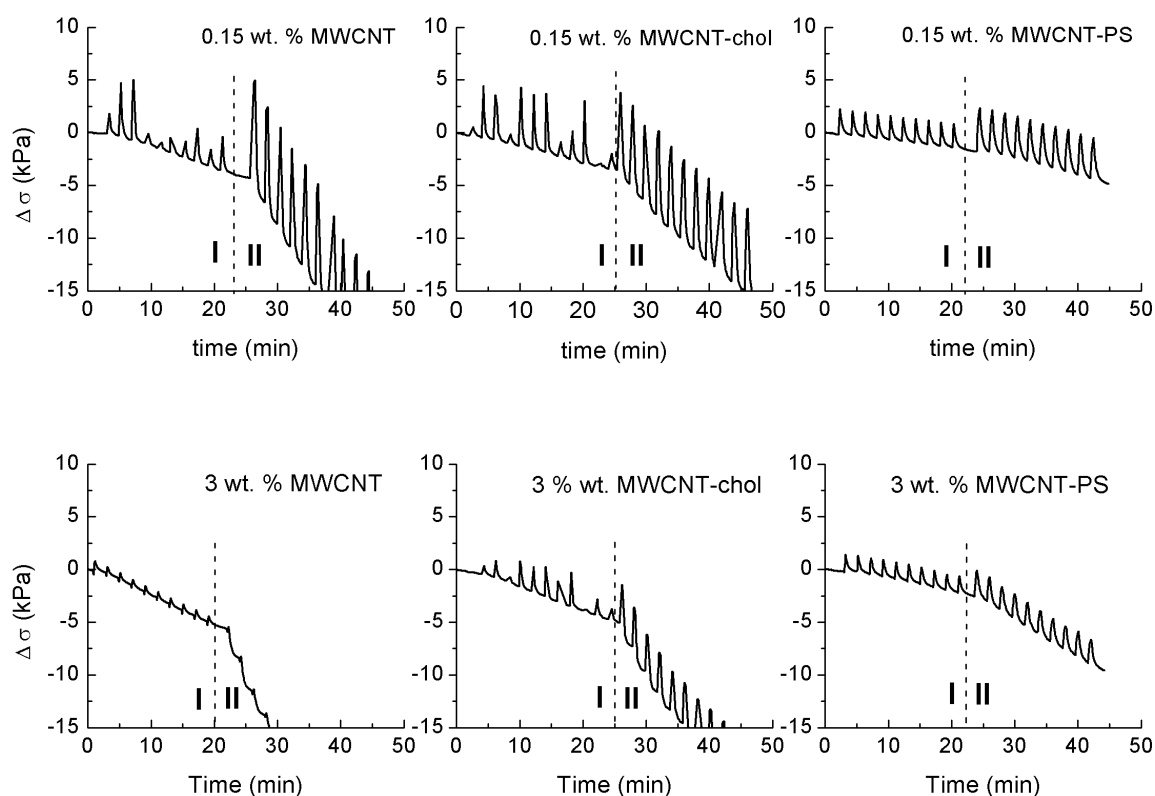


Fig. 12 Photo-actuation performance for CNT-based SIS elastomeric composites prepared by solution casting [38] (reproduced with permission)

From the previously mentioned results of modification and successful improvement of the photo-actuation performance by covalent modification, the new approach of the modification (Scheme 9) and also composite preparation was formulated. *In situ* approach described in section III was utilized and therefore significantly enhanced photo-actuation performance was obtained, due to the proper CNTs dispersibility in the PMMA-*b*-PBA-*b*-PMMA elastomer matrix (see Fig. 11). All these results have consequences in mechanical performance of the samples already described in section V (Fig. 10). In this case, the polymer diblock grafted from the CNTs surface preferentially interacts with soft PBA phase and due to this fact the soft



phase responsible mainly for the photo-actuation performance was stiffened, therefore mechanical response upon light stimulation was enhanced. Furthermore, heat transfer within the material was considerably improved due to proper dispersibility. Thus, it can be stated that covalent modification from the sustainability point of view is very promising approach resulting in the materials with promising real-life applications as photo-actuators.

## VII. CONCLUSIONS

Elastomeric composites presented in this book chapter were described from the CNTs modification point of view. Various modifications, such as simple covalent functionalization or non-covalent approach with low molecular weight substances as well as covalent modification with short homopolymer chains or diblock polymer chains were described. Furthermore, important section was focused on the preparation techniques, where melt mixing, solution mixing and *in situ* polymerization approach was effectively applied for the composite preparation containing elastomers and modified CNTs. Since elastomers based on chemically cross-linked structure have several drawbacks, modification of the CNTs significantly improved their processability. One part of this section describes the effect of modification of CNTs on their dispersibility as this is crucial factor influencing the final composite properties and also their potential applicability. Then various techniques for dispersion evaluation were briefly mentioned and indicate that none of them is absolute and they must be correlated to each other. Another section provides clear evidence about the impact of the CNTs modification on the morphology of the elastomeric materials mainly based on block copolymers because morphology of these ones is mostly affected. The last section of this chapter focused on the viscoelastic and electrical properties. Successful CNTs modification provides composite materials with improved dispersion. Two main theories were presented in more detail, the first theory claims that better dispersion subsequently improves viscoelastic and electrical properties, as traditional approach, while second theory claims that proper dispersion prolongs the conducting pathways created by CNTs in the composite and thus suppresses the electrical charge transport within the material. The aim of the last part of this book chapter is to improve the photo-actuation performance of the elastomeric composites. It was noted that various covalent modifications improve CNTs dispersion in the elastomer matrix resulting in better heat transfer and also due to the proper modifying agent with better interaction with the matrix and leads to the material stiffening. Therefore more stable elastomeric materials as well as composites with significantly enhanced photo-actuation performance, which can be achieved.

## ACKNOWLEDGMENT

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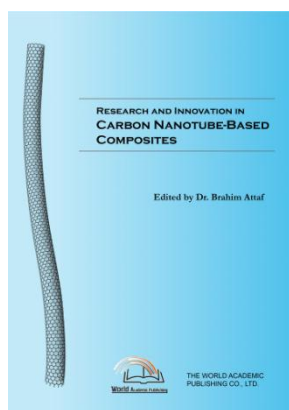
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## Research and Innovation in Carbon Nanotube-Based Composites

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This book of nanoscience and nanotechnology provides an overview for researchers, academicians and industrials to learn about scientific and technical advances that will shape the future evolution of composite materials reinforced with carbon nanotubes (CNTs). It involves innovation, addresses new solutions and deals with the integration of CNTs in a variety of high performance applications ranging from engineering and chemistry to medicine and biology. The presented chapters will offer readers an open access to global studies of research and innovation, technology transfer and dissemination of results and will respond effectively to challenges related to this complex and constantly growing subject area.

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