Photoactuating of Materials Designed for Haptic Aid-Tablets for Visually Impaired People Based on Styrene-b-Isoprene-b-Styrene Block Copolymer Nanocomposites

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I. Introduction

Actuation phenomenon is considered as materials ability to undergo reversible shape changes in response to an external stimulus [1, 2]. There were several trigger stimuli reported, such as the electric field, light, pH or temperature [2÷5]. The trigger-responsive materials find their employment in a wide range of applications comprising sensor, artificial muscles etc [1, 2]. The photo-responsive materials poses compared to other stimuli several advantages, where the low energy consumption compare to heat and avoiding high voltages compared to electrical principles [6].

Generally, the actuating materials can be pure polymers or polymer composites. In both cases, the energy absorbers-triggers and assembling structures need to be present in materials [7]. However, the actuation may be improved by addition of an energy trigger. As an energy absorbers, dyes [8] or carbon based fillers were reported [9, 10]. In 1999 Zhang and lijima reported actuation of single walled carbon nanotubes, which were able to stretched, bend and recover repeatedly when exposed to light [11]. The effect was more pronounced, when majority of them was aligned in preferred direction [12]. Various polymer matrices were filled by the carbon nanotubes and tested as photoactuators. Widely polyurethane based thermoplastic elastomers [2, 13, 14], poly(dimethyl siloxanes) [6], liquid crystal elastomers [10, 15], or styrene-b-isoprene-b-styrene and ethylene vinyl acetate thermoplastic elastomers were studied [16].

Recently the photo-responsive materials find their utilization at development of visual-aid tactile displays for blind or partially-sighted people within the Nano-optical mechanical system (NOMS) project [17]. Within this project, the eight research teams from the whole Europe were interested. Besides material scientists also neurologists and people from blind community cooperated to fabricate microsystems capable of light-induced mechanical actuation. The new developed systems should provide fast-refreshable, portable tactile displays to be able to represent complex images such as mathematical equations and graphs. The outcome of the project should not have impact only on the blind community. The everyday activities of the whole world population can be greatly improved by implementation such device into mobile phones, computers etc.

For wide industrial application, the price of the entrance matters plays a crucial role. This may become a limiting factor for otherwise well-behaving liquid crystals, which demanding synthesis makes them unattainable for industry. Also the two-component cross-linked systems, such PUR or PDMS poses some technological complications. The attention was therefore paid to the thermoplastic elastomer based materials. In this study the potential of SIS copolymer Kraton D1165 was tested. As well as others polymer matrices suffers from the lack of energy absorbers-trigger, therefore the

multiwalled carbon nanotubes were employed to make the material photo-actuating. As is generally considered, the homogeneity of the filler has a dramatic impact on the actuation ability. Therefore the surface of the carbon nanotubes was covalently modified either by cholesteryl chlororformate, which is an aliphatic branched low molecular substance, or with short polystyrene brushes, to ensure the well dispersed filler in the polymer matrix. The effect of the surface treatment was observed as well. The photoactuation was investigated by DMA in iso-strain mode at constant preload.

2. Experimental

2.1. Materials

The multiwalled carbon nanotubes (Nanocyl 7000, Belgium) were used. For better compatibility, with polymer matrix, their surface was covalently modified either with cholesteryl chlororformate (Nanocyl-chol) or grafted by short polystyrene chains (Nanocyl-PS) by ATRP according to the literature [18]. The structures of the modified MWCNT are shown in Scheme 1. A commercial styrene-b-isoprene-b-styrene copolymer (Kraton D1165, 30 % PS, the Netherlands) was supplied as pellets. The toluene (Microchem, Slovakia) was also used as received.

![Scheme 1. Covalently modified multiwalled carbon nanotubes with left) cholesteryl chlororformate (Nanocyl-chol), right) polystyrene (Nanocyl-PS)](image)

2.2. Methods

Composite preparation

The carbon nanotubes were dissolved in toluene (1.6 ml) and sonicated for 8 minutes. To achieve homogeneous material, the MWCNT were mixed with dissolved SIS (in 6.4 ml toluene) via using high speed blade shear mixing device at 1200 rpm device for two hours. The mixture was cast into Teflon chamber, the solvent was evaporated and the film was formed. The real amount of MWCNT used for composites preparation is listed in Table 1. The film was dried at room temperature and atmospheric pressure for four days. To ensure that all the solvent was removed, the films were subsequently placed into oven and heated form room temperature to 80 °C by 10 °C step per day. This temperature was kept and the pressure was decreased by 100 mbar per day and finally kept one day at 10 mbar.

![Composite preparation](image)
3. Results and discussion

3.1. Composite preparation and characterization

To obtain well-working photo-activating polymer composite materials based on carbon nanotubes, two basic requirements have to be accomplished. The carbon nanotubes have to be dispersed well and distributed homogeneously within the polymer matrix and the majority of them should be aligned in the direction of actuation [15, 19]. Therefore, the covalently modified carbon nanotubes either with cholesteryl chloroformate or short polystyrene chains were employed in this study. In both the types of prepared composites, the concentration of the carbon nanotubes was 1 wt. % in relation to the neat carbon nanotubes. The content of grafted polystyrene in Nanocyl-PS and content of cholesteryl in Nanocyl-chol was approximately 50 and 15 wt. %, respectively [18]. The composites were prepared by shear mixing of the viscous carbon nanotubes-polymer solution. The high shear forces produced at shear mixing ensure obtaining solution with well entangled and dispersed multiwalled carbon nanotubes [19]. The later requirement – the orientation- was achieved by pre-stretching of the composite stripes by using pre-stretching device. The aim of the above described procedure was to induce and freeze the orientation of carbon nanotubes as well as polymer chains in the elongation direction. The one direction-preferred orientation was proved by TEM.

In Figures 1 and 2, the TEM images of pre-stretched composites stripes are shown. The images in both longitudinal as well as perpendicular directions to the elongation were performed. For better visualization of the block copolymer phase separation, the samples were stained by OsO₄ vapours before analysis. In Figures 1 and 2 left can be seen that in both the composites the preferred orientation of carbon nanotubes was observed. The orientation direction is highlighted by the arrows. On the other hand, from the perpendicular cut samples, Figures 1 and 2 right, the round shape objects were detected, some of them are encircled. They can be attributed to the cross-sectioned MWCNTs or small clusters. In addition to well dispersed and distributed MWCNT, a presence of some clusters stacked probably on the metal catalyst was observed as well.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>MWCNT</th>
<th>Kraton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocyl-PS</td>
<td>0.0193</td>
<td>0.944</td>
</tr>
<tr>
<td>Nanocyl-chol</td>
<td>0.0163</td>
<td>0.967</td>
</tr>
</tbody>
</table>

To obtain well dimension-defined stripes, the cast composite foil was compressed moulded at 120 °C at pressure 40 kN for 10 minutes. The thickness of the final foil was 0.2 mm. The stripes (5 x 40 x 0.5 mm) were cut from the foil.

The pre-stretched composites stripes were prepared by using custom-made tightening device. The stripes were clamped into elongation device and stretched. The device with composite stripe was placed into oven heated at defined temperature for a certain time. After removal the device with stripe was cooled down by ice-cold water.

**Transmission electron microscopy**

The dispersion of carbon nanotubes as well as orientation was observed by transmission electron microscopy a Tecnai G2 Spirit Twin 12, FEI at 120 kV of electron beam acceleration. The samples were prepared by ultramicrotome (Ultracut UCT, Leica) under cryo-conditions (the sample and knife temperatures were -70 and - 45 °C, respectively). The ultra thin slides were transferred onto a carbon coated copper grid and stained with OsO₄ for 1 hour and 30 minutes in order to improve the visibility of the separated block of the copolymer.

**Photo-actuation by DMA**

The photoactuation of materials was tested by dynamic mechanical analyzer (Q 800, TA Instruments) in iso-strain mode at room temperature. The preload was 0.05 % or 15 %, the applied force was 0.04 N. The illumination of the samples was provided by red light emitting diode (LED; Luxeon Rebell, Philips) with emitting wavelength of 627 nm (58 mW), whereas the distance between the sample and the light source was approximately 8 mm.

**3.2. Photoactuation by DMA in iso-strain mode**

The actuation was monitored by DMA in iso-strain mode. The pre-stretched composite stripe was fixed into DMA clamps, pre-load and irradiated. The produced actuation stress was monitored as time-dependence in response to illumination. The set DMA pre-strain was 0.05% and 15% and the preload was 0.04 N. The clamped stripe was irradiated by red LED at 300 mA for 10 or 30 seconds and the changes in stress in time were recorded simultaneously. As a response to the light either negative stress, pointing to the elongation of the stripe, or positive values, corresponding to the contraction, were observed. The example of the obtained data for composite expansion is shown in the Figure 3. The sample was irradiated for 10 seconds and then 1 minute and 50 seconds was the laser source was switched off. These cycles were repeated ten times. Then the irradiation internal was increased to 30 seconds after them the laser was switched of for 1 minute and 30 seconds. During both the irradiation intervals, good reproducibility was obtained.
The pre-stretching temperature had influence on the induced orientation. Better actuation was observed when the samples were pre-stretched at lower temperature (Ent. 1 and 3). In addition the relative elongation during pre-stretching played a role as well. The values of actuation obtained for stripe elongated by 30 % were lower compared to the sample elongated by 50 % (Ent. 2 and 3). The effect of the presence of short PS chains, which act as softening agents, appears [18].

It was found that the most important during the photoactuation measurement was the pre-stretch set at DMA measurement. The contraction of the samples occurred just after increasing the pre-stretch up to 15 %, Table 2 ent. 5. Similar dependence of expansion versus contraction on the pre-stretch at DMA measurement has been described also by Terentjev et al. [10]. This group described for the carbon nanotubes (2 wt. %) composites of polydimethylsiloxane (PDMS) that the switch from expansion to contraction behavior was observed at the same pre-load of 15 %. The values of the actuation stress in expansion as well as contraction achieved here for Nanocyl-PS and Nanocyl-chol / SIS composite were comparable to those obtained previously for the PDMS composites [10]. However taking account the price and also technological processing, the Kraton based materials poses advantage. Since the PDMS is a two-component cross-linked system; it requires well controlled processing, what can be avoided when a thermoplastic-elastomer matrix, such as Kraton D1165 is used. Therefore SIS could be considered as a promising matter for development and large-scale production of haptic displays. Within the NOMS project, the systems employing both the contraction as well as expansion mechanisms were developed.

4. Conclusion

In this study, the actuation of styrene-b-isoprene-b-styrene based composite materials containing modified MWCNT is described. The influence of the pre-stretching conditions and DMA pre-load conditions on the actuation ability was studied. The materials exhibited either expansion or contraction in dependence on DMA pre-load conditions. The highest actuation stress was achieved at composite containing MWCNT covalently modified with cholesteryl groups pre-stretched at 70 °C. The actuation stress value reached 14 kPa after 30 s laser irradiation.

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Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Pre-stretching conditions; DMA pre-strain conditions</th>
<th>Δσ ± σ, (kPa) during irradiation by red LED; 58 mW</th>
<th>10 seconds Irradiation</th>
<th>30 seconds Irradiation</th>
<th>Expansion</th>
<th>Contraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nanocyl-chol 1 wt. % SIS</td>
<td>80 °C, 50 %, 5 min; 0.05%</td>
<td>3.1 ± 0.3; Expansion</td>
<td>4.7 ± 0.1; Expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nanocyl-chol 1 wt. % SIS</td>
<td>70 °C, 30 %, 5 min; 0.05%</td>
<td>8.5 ± 0.5; Expansion</td>
<td>11.0 ± 0.6; Expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Nanocyl-chol 1 wt. % SIS</td>
<td>70 °C, 50 %, 5 min; 0.05%</td>
<td>9.1 ± 0.4; Expansion</td>
<td>14.0 ± 0.1; Expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Nanocyl-PS 1 wt. % Kraton</td>
<td>70 °C, 50 %, 5 min; 0.05%</td>
<td>5.6 ± 0.2; Expansion</td>
<td>6.3 ± 0.1; Expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Nanocyl-PS 1 wt. % SIS</td>
<td>70 °C, 50 %, 5 min; 15 %</td>
<td>1.3 ± 0.2; Contraction</td>
<td>2.1 ± 0.3; Contraction</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

* after switching off the irradiation the samples were relaxed for 1 min 50 s before the light was again switched on.
Translation into English by the Authors

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