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Molecular dynamics simulation model for the photo-responsive polymer and its nanocomposites

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ABSTRACT

The photo-mechanical characteristics of highly crosslinked, photo-responsive polymer (PRP) is investigated using molecular dynamics simulation. By applying *trans*-to-*cis* photoactive potential to the classical polymer force field, both the microstructural transformation of each mesogen molecule and the bulk thermo-mechanical properties are quantitatively observed. Through the model, the contractions of bulk PRP material are clearly found both with thermal and optical signals, and their deformation quantities show good agreement with other reported experimental data. In particular, in this study we consider PRP/Au nanocomposite models that nano-sized (a diameter of 13-20 Å) spherical gold particles are fully dispersed in the polymer matrix. The models therefore can potentially be used to estimate the effect of nanoparticle doping on the photo-mechanical performances of the nanocomposite system.

1. INTRODUCTION

Shape memory polymer, a novel material which macroscopically deforms according to the programmed shape in response to external stimuli such as electrical voltage or temperature, has been studied in various fields because of its potential applicability for remotely controlled design parts of mechanical sensors and actuators. Among these shape-memorable materials, a photo-responsive polymer (PRP) has an especial and distinct characteristics in that the deformation event can be occurred by irradiation or specific wavelength of light (Yu 2003). The origin of photo-responsibility of the material is isomerization of the photoactive groups – such as azobenzene, azotolane, and diarylethene – in the mesogen molecules contained in the poly-structure. When the photoactive groups are exposed to the light, the molecular structure and the

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associated chemical bonding characteristics are significantly changed and it collapses the pre-ordered phase of surrounding polymer matrix if the absorbed light energy exceeds the phase transformation energy barrier of the aligned molecular structures (Finkelmann 2001).

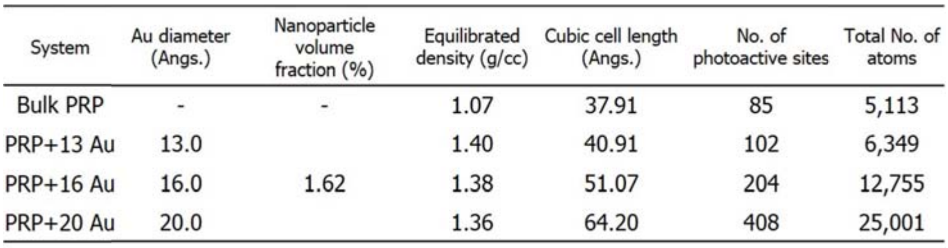
According to this, recently our research group developed a multiscale model for the PRP structure which predicts its opto-mechanical behavior considering with the fundamental physics of the photo-responsive mechanism of azobenzene polymer by combining first principle calculation, molecular dynamics (MD) simulation and nonlinear continuum mechanics (Yun 2015, Choi 2014, Chung 2015). In this paper, we extend our previous MD work (Choi 2014) to nanocomposites system doped with nano-sized spherical gold particle. Thus, the possibility on the enhancement of thermal and mechanical stability of PRP material has been estimated, sustaining with the inherent photo-deformation properties of bulk resin.

2. MOLECULAR DYNAMICS

2.1 Modeling of photo-responsive polymer (PRP) and PRP/Au nanocomposites

To construct the condensed polymer structure via MD simulations, we used a commercial MD software (Materials Studio 6.0, Accelrys Inc.) as well as open source-code (LAMMPS, Sandia Lab.). The model contained azobenzene groups both in the host and guest molecules of polymer chain. All the mesogens were aligned along x direction and highly crosslinked. Together with neat (bulk) PRP model obtained from our previous work (Choi 2014), in this study we considered three different unit cells which contain different diameters of spherical gold nanoparticle in the center of the unit cell respectively but have same loading condition (1.62 vol.%). All the considered models were thermodynamically equilibrated under NVT (300K for 300ps) and NPT (0.1MPa and 300K for 1.5ns) ensemble run. The details of geometry and size of the modeled unit cell are described in **Table 1**. Five different isomerization ratio ($n_{isomerized}$ = 0.00, 0.25, 0.50, 0.75, and 1.00) of azobenzene group in the unit cell were considered by combining the photoactive dihedral potential for C-N=N-C suggested by Heinz et al. (Heinz 2008) with classical forcefield (PCFF) to each equilibrated model.

Table 1 Details of PRP and PRP/Au nanocomposites models considered in this study



System	Au diameter (Angs.)	Nanoparticle volume fraction (%)	Equilibrated density (g/cc)	Cubic cell length (Angs.)	No. of photoactive sites	Total No. of atoms
Bulk PRP	-	-	1.07	37.91	85	5,113
PRP+13 Au	13.0	1.62	1.40	40.91	102	6,349
PRP+16 Au	16.0		1.38	51.07	204	12,755
PRP+20 Au	20.0		1.36	64.20	408	25,001

2.2 Photostrain and thermomechanical properties

Fig. 1 shows the photostrain of modeled nanocomposites according to the isomerization ratio of azobenzene. The photostrain was defined as the shrinkage of the unit cell along nematic direction after the photoactive potential was applied to the equilibrated unit cell. Similar with the neat PRP model, monotonic contractions of the unit cell length along nematic direction are clearly observed for all the considered PRP/Au nanocomposites models. Especially, because the spherical nanoparticle does not inhibit the mobility of far-field polymer matrix, the maximum contraction size of PRP/Au nanocomposites is quite similar or even higher than the neat PRP. To further discuss on this, we estimated the mechanical stability (axial stiffness) as well as thermal stability (melting temperature during heating-up simulation) of the modeled PRP/Au nanocomposites during the isomerization, and the results are shown in **Fig. 2** and **Table 2**, respectively. As the *trans*-state of azobenzene is transformed into *cis*-state due to the isomerization, the directionality of mesogen molecules becomes weaker and the material changes from transversely isotropic to isotropic. Regardless of the isomerization ratio, the nanocomposites models have improved material properties both for axial stiffness (up to 26%) and melting temperature (up to 8.5%) comparing with the ones of neat PRP model. One remarkable thing is that during the photo-isomerization of azobenzene, the stiffness components along the transversal direction against the mesogen are nearly constant whereas the corresponding one of neat PRP model is slightly recovered. It indicates the existence of anchoring effect on the nanoparticle surface for the surrounding mesogen and methyl polymer chains.

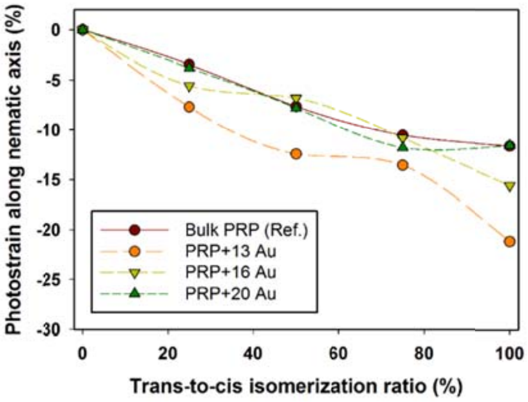


Fig. 1 Photostrain of the modeled PRP/Au nanocomposites.

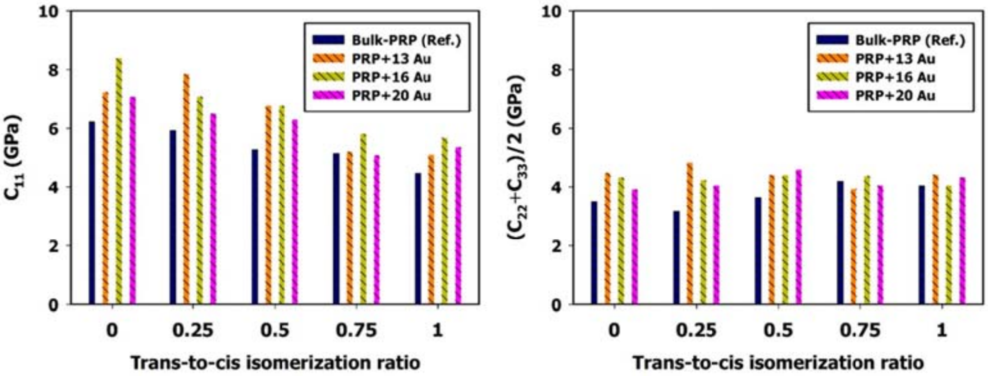


Fig. 2 Elastic stiffness components of modeled PRP/Au nanocomposites

Table 2 Melting temperature of PRP/Au nanocomposites (gold diameter: 20Å)

Isomerization ratio	T_{iso} of Bulk PRP (Ref.)	T_{iso} of PRP+20 Au model
- (trans-AZ)	462.0K	**479.5K**
0.25	425.0K	**454.0K**
0.50	381.5K	**414.0K**
1.0 (full cis-AZ)	363.5K	**370.0K**

3. CONCLUSIONS

In this study, we modeled a PRP/Au nanocomposites system via MD simulations and examined the effect of gold nanoparticle doping on the enhancement of thermo-mechanical properties of the bulk PRP resin. Comparing with the neat PRP model, the considered nanocomposites models have superior elastic stiffness along normal directions and higher thermal stability because of the strong atomic interaction between gold nanoparticle and surrounding mesogen molecules. As the photo-isomerization of azobenzene is progressed, the orientational order of the internal molecular structure of the unit cell are decreased and the material properties become from transversely isotropic to isotropic, both for the neat PRP and PRP/Au nanocomposites models. But the maximum contraction size of PRP/Au nanocomposites is comparable or even larger than the neat PRP model, verifying that the opto-mechanical behavior of the material is not degraded if the gold nanoparticles are well-dispersed in the resin.

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