## CHAPTER VI

## CONCLUSIONS AND RECCOMENDATIONS

The present work was focused on the development of polyoxymethylene (POM) and its copolymer based nanocomposite and nanofiber materials. For POM nanocomposites, the work clarified the effects of surfactants used for modifying of clay on the intercalation of the polymer chain as well as the properties of the nanocompoites obtained. A quaternary ammonium surfactant initiated the mixture of intercalated/flocculated nanocomposite structure while a primary ammonium surfactant initiated the exfoliated structure of the nanocomposites, which induced an improvement in mechanical and gas barrier properties. The organo-modified bentonites, acting as a nucleating agent, generated numerous nucleating sites with anisotropic crystallite growth. POM/organo-modified bentonite nanocomposites were found to be more elastic than the pristine POM at low frequency (below $1 \mathrm{rad} / \mathrm{s}$ ) while showing less elasticity than the pristine POM with frequencies in the range of $10-100 \mathrm{rad} / \mathrm{s}$. The degradation of POM was accelerated by the presence of the organo-modified bentonites, owing to the acid protons generated during the thermal degradation of the organo-modified bentonite.

In order to achieve fine fiber, the work considered electrospinning technique as it is known as a way to produce fine fiber with diameters ranging from nano- to micro-scale. An electrospun polyoxymethylene (POM) nanofiber using a hexafluoroisopropanol (HFIP)-based solvent was successfully prepared by controlling the spinning conditions (i.e. electrostatic field strength and relative humidity) and the polymer/solvent properties (i.e. copolymer content and vapor pressure of the solvent). Nanoporous structure was inevitably formed and was mainly induced via thermally induced phase separation (TIPS) and vapor induced phase separation (VIPS) mechanisms. A decrease of nanoporosity could be achieved under (i) an increase of the oxyethylene unit in the POM copolymer, (ii) a decrease of solvent vapor pressure, (iii) an increase of spinning voltage, and (iv) a decrease of relative humidity.

The study also covered the fiber structure at the molecular level based on the detailed analysis of X-ray diffraction and polarized infrared spectra of POM
nanofibers, opening a new concept of electrospinning method for controlling the crystal morphology and molecular orientation of nanofibers. By controlling the electrical voltage and the rotating velocity of the disc collector, the morphology was interchangeable between an extended chain crystal (ECC) and a folded chain crystal (FCC). Molecular orientation parallel to the fiber axis was observed in both isotropic and anisotropic POM nanofibers. The high rotating disc velocity was not only inducing the ECC morphology but also enhancing the polymer chains to be parallel to the fiber axis. Based on Herman's orientation and crystallite size estimated from the 100 and 009 reflections, it was clear that, at the highest rotating speed (1890 $\mathrm{m} / \mathrm{min}$ ), nanofibril aligned almost parallel to the fiber axis with a bundle of about 14 polymeric chains and ca. 40 monomeric units under $9 / 5$ helical structure. The present work demonstrated a new approach to control crystal morphology and molecular orientation by producing nanofibers via electrospinning process with a rotating disc collector.

The future work for POM/organoclay nanocomposites is to achieve the better miscibility between organoclay and POM chains by modifying of silicate clay using silane coupling agent with an oxymethylene- or oxyethylene-like unit. For electrospun POM nanofiber, the crystallization of polymer affected by the shear inducing during the electrospinning process, which may favor the difference in shish kebab morphology, is another important point needed to clarify. An observation of tie chains connecting neighboring lamellae is also another important point needed for consideration. The amount of which may be increased by increasing of shear rate.

