SYNOPSIS

Nanomaterials are defined as materials with at least one external dimension in the size range from approximately 1-100 nanometers. Nanoparticles, in particular, are nanomaterials with all three external dimensions at the nanoscale. Two principal factors that cause the properties of nanomaterials to differ significantly from other materials and make them unique are: i) increased relative surface area, and ii) quantum effects. These factors can significantly change or enhance properties, such as reactivity, strength, optical and electrical characteristics. Hence, metal nanoparticles are currently being explored for their versatile applications as catalysts [1], chemical and bio sensors [2, 3] and drug delivery systems [4]. Noble metal nanoparticles, such as those of Gold and Silver, possess bright color in aqueous solutions [5] and are potentially useful as biosensors and for biological imaging. Spectrophotometric detection of various molecules/species, based on the optical properties of metal nanoparticles, has been widely reported [6]. Change in the spectral position, FWHM or intensity of absorption spectra of nanoparticles, due to interaction of metal nanoparticles with biological analytes, is the basis of these widely applicable and convenient colorimetric sensing techniques [7].

Metal nanoparticles, or any other fillers in the nanoscale regime, when incorporated into a polymer matrix, give rise to a new class of materials known as polymer-nanocomposites. Typically, the structure is a matrix-filler combination where the fillers like particles, fibers, or fragments surround and bind together as discrete units in the matrix. These advanced materials offer enhanced mechanical, thermal, flame retardant, barrier, electrical and chemical properties compared to their constituent elements. In recent years, nanocomposites have generated much research interest owing to remarkable enhancements in the various composite properties at very low volume fractions of nanofillers [8-10]. These polymer nanocomposite materials have found application in fields as diverse as laser safety
goggles, scratch resistant materials, aerospace, automotive sector for interior parts and under-the-hood applications, and so on.

Compared to conventional methods of fabrication, the major advantages of using high energy radiation, including electron beam and gamma irradiation, for synthesizing metal nanoparticles and nanocomposite materials, are that these are room temperature, pollution-free and high efficiency processes that can be used for rapid synthesis of uniformly dispersed metal nanoparticles [11, 12]. Similarly, in case of polymer nanocomposites, ionizing radiations have been found to impart long service life, uniform and high degree of cross-linking, and excellent thermo-mechanical properties to the materials [13, 14].

The present study is aimed at the investigation of application of ionizing radiations, viz., $^{60}$Co gamma, electron beam and synchrotron radiations for fabrication of noble metal nanoparticles (Au and Ag) and novel inorganic/organic polymer nanocomposite materials. The applications of these materials in the field of sensors, optical limiters and flame retardants have also been discussed. Details of the work done and results have been reported in following five chapters.

Chapter 1: Introduction: Metal nanoparticles and polymer nanocomposites, basic principles of ionizing radiation and radiation induced synthesis

The chapter deals with fundamental aspects related to metal nanoparticles, polymer nanocomposites (PNCs) and radiation technology. These include an understanding of the basis of classification of nanoparticles and nanocomposite materials. The principles behind the stabilization of metal nanoparticles in aqueous solutions and the unique optical properties of noble metal nanoparticles, which are used in sensor applications, have been discussed. Basic aspects of radiation chemistry, such as the types and energies of ionizing radiation and
their interactions with different media have also been delved into. The radiation chemistry of aqueous solution is discussed in details, starting from the typical time scales of different radiolytic events, which finally lead to formation of primary as well as secondary radiolytic species. The chapter also deals with the conventional methods of nanoparticles and PNCs fabrication, and the advantages offered by radiation technology over these techniques. The applications of the radiation synthesized materials in the field of sensors, optical limiters and flame retardants are also mentioned.

Chapter 2: Experimental Methodology and characterization techniques

During the course of this study, a variety of methods have been employed to synthesize nanomaterials, including nanoparticles and polymer nanocomposites, and their characterizations have been carried out using numerous characterization techniques. These include steady-state irradiation facilities, such as $^{60}$Co gamma chamber, Electron beam and Synchrotron irradiators for irradiation, and characterization techniques such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), X-ray Scattering (SAXS and XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Analysis (TGA and DSC), UV-visible Spectroscopy, etc.. The chapter discusses the principles and methodologies involved in these studies.

Chapter 3: Gamma radiolytic synthesis of Poly(N-vinyl-2-pyrrolidone) capped Au nanoparticles for sensor applications

$^{60}$Co-gamma radiation was used to carry out radiolytic synthesis of Gold nanoparticles (Au-NPs) in aqueous solutions, in presence of Poly(N-vinyl-2-pyrrolidone) (PVP) as the capping and stabilizing agent. Reactive transient species generated through water radiolysis include solvated electrons ($e_{aq}^-$) and isopropyl radicals (generated from the reaction between
OH/H and isopropanol present in the reaction mixture), which are responsible for the reduction of the precursor Au\(^{3+}\) ions to Au atoms in the zero-valent state (Au\(^0\)). The Au\(^0\) thus formed coalesce to form small nuclei, which grow to Au nanoparticles. The effect of variation of parameters, such as radiation dose, precursor ion concentration, stabilizer molecular weight and concentration, etc., on the particle morphology was studied. The saturation dose for complete reduction of \(5.0 \times 10^{-4}\) mol.dm\(^{-3}\) Au\(^{3+}\) was determined spectrophotometrically to be 1.8 kGy. The reaction parameters were optimized to fabricate uniformly dispersed, spherical nanoparticles with average particle size in the range of 9-12 nm (PVP of molecular weight 360 kDa as the capping agent), as determined by TEM analysis. The Au nanoparticles thus engineered were found to exhibit typical Localized Surface Plasmon Resonance (LSPR) band at ~530nm. This optical property of the PVP-Au-NPs was exploited for employing these Au-NPs as optical biosensors.

The PVP-Au-NPs system synthesized using PVP with molecular weight 360 kDa as the capping agent was used for detection and estimation of a biologically relevant analyte hydrogen peroxide. The detection principle was based on spectrophotometrically monitoring the enzymatic reaction of H\(_2\)O\(_2\) with o-phenylene diamine (o-PDA) in presence of enzyme Horse radish peroxidase (HRP). The reaction product has a weak absorption in the yellow region of the spectrum. Interaction of the reaction product with PVP-Au-NPs leads to an enhancement in the intensity of the LSPR absorption band of PVP-Au-NPs. The detection limit was determined to be \(1.0 \times 10^{-7}\) mol.dm\(^{-3}\) and H\(_2\)O\(_2\) concentration could be estimated from \(1.0 \times 10^{-7}\) mol.dm\(^{-3}\) to \(2.0 \times 10^{-4}\) mol.dm\(^{-3}\) by choosing appropriate experimental parameters. Silver nanoparticles, fabricated via a similar protocol, displayed an LSPR band at ~420 nm which overlapped with the absorption band of the reaction product leading to interference in the detection technique. The Ag nanoparticles were, therefore, ineffective in the estimation of H\(_2\)O\(_2\) by this method.
In another application, the same system, with some variation in the reaction parameters, was used for the detection and estimation of trace levels of Hg$^{2+}$ ions in aqueous solutions. The detection principle was based on the preferential interaction of Hg$^{2+}$ with PVP, a soft acid-soft base type of interaction. This leads to weakened interaction of the PVP capping agent with the Au-NPs, which gets manifested as a decrease in the LSPR band intensity of the Au-NPs. The use of low molecular weight PVP (40 kDa), as the capping agent, ensured that the Au nanoparticles were not highly stable and thereby, susceptible to changes in the external environment. This nanoparticle system was successfully used to estimate Hg$^{2+}$ within a concentration range of 0-500nM and demonstrated high selectivity towards Hg$^{2+}$ ions. The method was found to be independent of interference from other metal ions, such as Ca$^{2+}$, Cu$^{2+}$, Cd$^{2+}$ and Fe$^{2+}$ up to a concentration of 500 nM. Effect of parameters, such as pH of the medium, molecular weight and concentration of stabilizing agent on the detection efficiency were also studied in detail.

Chapter 4: A comparative study of the synthesis of Poly(N-vinyl-2-pyrrolidone) capped Ag nanoparticles by different radiation sources: application for estimation of uric acid.

In this study, Poly(N-vinyl-2-pyrrolidone) capped Ag nanoparticles (PVP-Ag-NPs) were fabricated using different radiation sources, namely $^{60}$Co-gamma, electron beam and synchrotron. All three radiation sources, though ionizing in nature, vary in their energies, depths of penetration and type of interaction with materials. The $\lambda_{\text{max}}$ for LSPR band of PVP-Ag-NPs was observed to be red shifted in the range of 420-430 nm with increase in Ag$^+$ concentration in case of X-ray and $\gamma$-irradiation method. However, $\lambda_{\text{max}}$ in case of electron beam irradiation method was blue shifted within the range 420-400 nm. In all three cases, effect of the concentration of PVP and Ag$^+$ ions on the optical properties of PVP-Ag-NPs
was also studied. As observed from TEM analysis, the Ag nanoparticles obtained by all three methods were uniformly dispersed and spherical in nature. However, the particle sizes could be fine tuned by suitably varying the reaction parameters or by changing the radiation sources.

Ag nanoparticles synthesized via the gamma radiolytic route were used as an optical biosensor for estimation of uric acid in biological samples. The PVP-Ag-NPs were thoroughly characterized and subsequently employed as LSPR-based optical sensors for detection and estimation of uric acid concentrations in human serum and bovine serum samples. The detection principle was based on the enzymatic degradation of uric acid in presence of enzyme uricase, leading to in situ formation of $\text{H}_2\text{O}_2$, which was responsible for partial oxidation/degradation of the PVP-Ag-NPs. The change was manifested as a decrease in the LSPR band intensity of the PVP-Ag-NPs. This technique was employed to successfully estimate uric acid in the concentration range of 0-50µM. Au nanoparticles, when employed for the same detection method, were found to display a slower response owing to their much greater noble character compared to Ag nanoparticles. Hence, the detection efficiency could be directly linked to the type of nanoparticle being utilized for the purpose.

**Chapter 5: Radiation induced fabrication of metal nanoparticles/inorganic fillers based polymer nanocomposite films for optical limiting and flame retardant applications**

Inorganic-Organic hybrid nanocomposite materials have received great attention from the industrial community because of their wide range of novel physico-mechanical properties. This chapter deals with the fabrication of metal nanoparticles and inorganic fillers based polymer nanocomposite films with potential optical limiting and flame retardant applications.
Nanocomposite films containing in situ generated Ag nanoparticles (Ag-NPs) dispersed in an Aliphatic urethane acrylate (AUA) matrix were synthesized using electron beam curing technique, in presence of an optimized concentration of Ag\(^+\) precursor ion and a diluent Trimethylolpropanetriacrylate (TMPTA). The reactive diluent not only made processing of the oligomer easier by suitably lowering its viscosity but also played the role of an effective crosslinker for AUA. The Ag-NPs-polymer nanocomposite films were thoroughly characterized by UV-visible spectroscopy, TEM and FE-SEM techniques. Both TEM and FE-SEM revealed formation of well dispersed, spherical Ag-NPs of size range 5-10 nm within the AUA-TMPTA polymer matrix. Ag-NPs doped polymer films showed an absorption peak at ~420nm whose intensity increased with increase in the Ag\(^+\) ion concentration. The optical limiting property of the Ag-NPs- polymer nanocomposite films was tested using a Nd-YAG Laser operated at third harmonic wavelength of 355nm. For a 25ns pulse and 10 Hz cycle, films showed good optical limiting property and the threshold fluence for optical limiting was found to be ~3.8 J/dm\(^2\), for exposure duration of 10 seconds. The dynamic range was calculated to be 22.3, while transmission decreased by 82%. The presence of additional fillers, such as thiophene and modified clay cloisite 30B in addition to Ag nanoparticles, on the optical limiting characteristics was also studied.

Polymer clay nanocomposite (PCN) films were fabricated by uniformly dispersing organically modified montmorillonite clay (Cloisite 20A and Cloisite 30B) in varying concentrations of 2%, 5%, 10% and 15% (w/w), in an optimized composition of AUA-TMPTA mixture by ultra-sonication, followed by gamma radiation induced curing process. Radiation doses were optimized to obtain non-tacky, homogeneous films. The PCN films were characterized and evaluated for different properties, such as gel fraction, water uptake, solvent resistance, gloss at 60\(^\circ\) and pendulum hardness. For PCNs with both cloisite 20A and 30B as filler, clay loadings up to 5% showed increase in gel fraction compared to the neat
polymer film, above which the gel fraction was found to decrease gradually with the increase in filler loading. Clay loading of 2% was observed to be the optimum value to achieve maximum extent of crosslinking in both cases. Gloss of the PCN films decreased while the hardness increased with increase in the clay loading in the PCN films. The flame retardant behaviour of the PCN films was evaluated in terms of their Limiting Oxygen Indices (LOI), which, in turn was determined from the % char yields of the samples determined from the thermogravimetric analyses data. The LOI values recorded were found to be higher than 21 (the threshold value for flame retardancy) for all the PCN samples, with those containing 15% of modified clay cloisite 20A and cloisite 30B showing LOI values higher than 26, suggesting their potential application as effective flame retardant materials.

Summary

Present thesis describes results from the research work carried out towards radiation engineering and characterization of polymer stabilized metal nanoparticles and polymer nanocomposite materials using $^{60}$Co-gamma, Electron beam and Synchrotron radiation sources. Effect of variation of different reaction parameters on the material properties was thoroughly studied and accordingly optimized to obtain nanoparticles and polymer nanocomposites with desired properties. Radiation engineered PVP capped Au nanoparticles based optical sensors were used for detection and estimation of trace levels of hydrogen peroxide and mercury ions in aqueous solutions in micromolar and nanomolar concentrations, respectively. Similarly, a PVP-Ag nanoparticles based optical biosensor was designed for uric acid estimation in aqueous and serum samples within the concentration range of 0-50µM. Ag nanoparticles were also generated in situ in polymer matrices via radiation curing process to develop polymer nanocomposite films with potential optical limiting applications. Radiation curing technique was also employed to fabricate organophilic clay based inorganic-
organic nanocomposite materials having good flame retardant properties. The study thus inferred that new efficient materials for targeted applications can be engineered using radiation technology; an upcoming, clean, environment friendly and high throughput technology.

References


14. V. Kumar, Y. K. Bhardwaj, S. Sabharwal, Coating characteristics of electron beam cured bisphenol A diglycidyl ether diacrylate resin containing 1,6-hexanediol diacrylate on wood surface, 2006, Prog. Org. Coat. 55, 316-323.
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**Figure 3.2** TEM image of Au nanoparticles prepared using PVP of molecular weight 3,60,000 Da

**Figure 3.3** Absorption spectra of aqueous Au nanoparticle solution obtained for Au$^{3+}$ concentration (a) $1\times10^{-4}$, (b) $2.5\times10^{-4}$, (c) $4\times10^{-4}$, (d) $8\times10^{-4}$, (e) $1\times10^{-3}$ mol.dm$^{-3}$

**Figure 3.4** Absorption spectra of $4\times10^{-4}$ mol.dm$^{-3}$ aqueous Au nanoparticle solution (a) in presence of acetone and (b) in absence of acetone

**Figure 3.5** Absorption spectra of aqueous Au nanoparticle solution ($4\times10^{-4}$ mol.dm$^{-3}$) obtained in presence of (a) 0, (b) $6\times10^{-5}$, (c) $1\times10^{-4}$, (d) $1.5\times10^{-4}$, (e) $2\times10^{-4}$, (f) $3\times10^{-4}$, (g) $4\times10^{-4}$ mol.dm$^{-3}$ Ag$^+$ ions

**Figure 3.6** Absorption spectra of aqueous Au nanoparticle solution obtained for PVP concentration (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2%

**Figure 3.7** Absorption spectra of aqueous Au nanoparticle solution obtained for PVP of molecular weight ($M_w$) (a) 40,000Da, (b) 1,60,000Da, (c) 3,60,000Da

**Figure 3.8** Enzymatic oxidation of OPD

**Figure 3.9** Absorption spectra of reaction medium containing OPD, HRP, H$_2$O$_2$ and Au nanoparticles (in PVP, $M_w = 3,60,000$) in citrate buffer with varying H$_2$O$_2$ concentration (higher range of H$_2$O$_2$ concentration) (a) 0, (b) $2.5\times10^{-6}$, (c) $5\times10^{-6}$, (d) $1\times10^{-5}$, (e) $2.5\times10^{-5}$, (f) $5\times10^{-5}$, (g) $7.5\times10^{-5}$, (h) $1\times10^{-4}$, (i) $1.3\times10^{-4}$, (j) $1.6\times10^{-4}$, (k) $2\times10^{-4}$ mol.dm$^{-3}$ (Inset: Linear plot of absorbance at 427nm vs H$_2$O$_2$ concentration incase Au nanoparticle used was
in PVP of molecular weight (a) 3,60,000Da (R=0.9986), (b) 1,60,000Da (R=0.9981), (c) 40,000Da (R=0.9981): H₂O₂ concentration range= 2.5×10⁻⁶ to 2×10⁻⁴ mol.dm⁻³

**Figure 3.10** Absorption spectra of reaction medium containing OPD, HRP, H₂O₂ and Au nanoparticles (in PVP, M_w = 3,60,000) in citrate buffer with varying H₂O₂ concentration (lower range of H₂O₂ concentration) (a) 0, (b) 1×10⁻⁷, (c) 3×10⁻⁷, (d) 6×10⁻⁷, (e) 1.2×10⁻⁶, (f) 1.8×10⁻⁶, (g) 2.5×10⁻⁶, (h) 3×10⁻⁶, (i) 5×10⁻⁶ mol.dm⁻³ (Inset: Linear plot of absorbance at 427nm vs H₂O₂ concentration incase Au nanoparticle used was in PVP of M_w = 3,60,000 Da(R=0.9954): H₂O₂ concentration range= 1×10⁻⁷ to 3×10⁻⁶ mol.dm⁻³)

**Figure 3.11** TEM images of PVP-Au-NPs in (a) absence of Hg²⁺ ions (b) immediately after addition of 500nM Hg²⁺ (c) 5 minutes after addition of Hg²⁺

**Figure 3.12** Particle size analysis of Au nps in (a) absence of Hg²⁺ ions and (b) immediately after addition of 500nM Hg²⁺

**Figure 3.13** Absorption spectra of Au nanoparticle solution in presence of (a) 0 (b) 100 (c) 200 (d) 300 (e) 400 and (f) 500nM Hg²⁺ ion. (Inset: Calibration plot of Hg²⁺ ion concentration.)

**Figure 3.14** Absorption spectra of Au nps-500nM Hg²⁺ reaction mixture at pH (a) 3.0 (b) 6.0 (c) 8.0 (d) 10.0 and (e) 11.0

**Figure 3.15** Relative change (%) in OD of reaction mixture containing PVP-Au-NPs and 500nM Hg²⁺ ions as a function of PVP % (w/v)
(Inset: Relative change (%) in OD of reaction mixture containing PVP-Au-NPs and 500nM Hg$^{2+}$ ions as a function of PVP molecular weight).

**Figure 3.16** Interference study: Absorption spectra of Au nps in (a) absence of metal ions (b) 500nM Ca$^{2+}$ (c) 500nM Cu$^{2+}$ (d) 500nM Fe$^{2+}$ (e) 500nM Cd$^{2+}$ and (f) mixture of ions (500nM each)

**Figure 4.1** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different irradiation time: (a) 12s, (b) 23sec, (c) 41s, (d) 63s; [Ag$^+$]= 2X10$^{-4}$ mol.dm$^{-3}$, [PVP]= 0.5%, [Isopropanol]= 2X10$^{-1}$ mol.dm$^{-3}$, dose rate= 113.7kGy.h$^{-1}$.

**Figure 4.2** TEM image of Ag nanoparticles in PVP prepared by X-ray irradiation

**Figure 4.3** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by $\gamma$-irradiation for different absorption dose: (a) 1kGy, (b) 1.3kGy, (c) 1.6kGy; [Ag$^+$]= 2X10$^{-4}$ mol.dm$^{-3}$, [PVP]=0.5%, [Isopropanol]= 2X10$^{-1}$ mol.dm$^{-3}$, dose rate=4.0kGy.h$^{-1}$

**Figure 4.4** TEM image of Ag nanoparticles in PVP prepared by $\gamma$-irradiation

**Figure 4.5** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different Ag$^+$ concentration: (a) 1X10$^{-4}$ mol.dm$^{-3}$, (b) 2X10$^{-4}$ mol.dm$^{-3}$, (c) 3X10$^{-4}$ mol.dm$^{-3}$, (d) 4X10$^{-4}$ mol.dm$^{-3}$; dose = 1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]=2X10$^{-1}$ mol.dm$^{-3}$, dose rate= 113.7kGy.h$^{-1}$

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**Figure 4.6** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by $\gamma$-irradiation for different Ag$^+$ concentration: (a) $1 \times 10^{-4}$ mol.dm$^{-3}$, (b) $2 \times 10^{-4}$ mol.dm$^{-3}$, (c) $3 \times 10^{-4}$ mol.dm$^{-3}$, (d) $4 \times 10^{-4}$ mol.dm$^{-3}$; dose=1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]=2X10$^{-1}$ mol.dm$^{-3}$, dose rate= 4.0kGy.h$^{-1}$

**Figure 4.7** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB-irradiation for different Ag$^+$ concentration: (a) $1 \times 10^{-4}$ mol.dm$^{-3}$, (b) $2 \times 10^{-4}$ mol.dm$^{-3}$, (c) $3 \times 10^{-4}$ mol.dm$^{-3}$, (d) $4 \times 10^{-4}$ mol.dm$^{-3}$; dose=1.0kGy, 2.0kGy, 3.0kGy, 4.0kGy respectively; [PVP]= 0.5%, [Isopropanol]=2X10$^{-1}$ mol.dm$^{-3}$, dose rate= 2.0kGy/pass

**Figure 4.8** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by X-ray irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); [Ag$^+$]= 2X10$^{-4}$ mol.dm$^{-3}$, [Isopropanol]=2X10$^{-1}$ mol.dm$^{-3}$, dose=2.0kGy, dose rate=113.7kGy.h$^{-1}$

**Figure 4.9** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by $\gamma$-irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); [Ag$^+$]=2X10$^{-4}$ mol.dm$^{-3}$, [Isopropanol]= 2X10$^{-1}$ mol.dm$^{-3}$, dose=2.0kGy, dose rate=4.0kGy.h$^{-1}$

**Figure 4.10** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB-irradiation for different PVP concentration: (a) 0.1%, (b) 0.5%, (c) 1%, (d) 2% (w/v); [Ag$^+$]=2X10$^{-4}$ mol.dm$^{-3}$,
[Isopropanol] = 2 \times 10^{-3} \text{ mol.dm}^{-3}, \text{ dose} = 2.0 \text{ kGy}, \text{ dose rate} = 2.0 \text{ kGy/pass}

**Figure 4.11** Absorption spectra of aqueous Ag nanoparticles in PVP prepared by EB-irradiation for different absorption dose rates: (a) 2.0 kGy/pass, (b) 1.0 kGy/pass; [Ag\(^+\)] = 2 \times 10^{-4} \text{ mol.dm}^{-3}, [PVP] = 0.5\%, [Isopropanol] = 2 \times 10^{-1} \text{ mol.dm}^{-3}

**Figure 4.12** Enzymatic degradation of uric acid in presence of Uricase.

**Figure 4.13** Absorption spectra of 150 µM Ag nanoparticle solution in presence of 50 µM uric acid after (a) 0 min, (b) 5 min, (c) 20 min, (d) 45 min, (e) 60 min. Inset: absorbance strength of Ag nanoparticles solution containing uric acid as a function of time.

**Figure 4.14** Absorption spectra of uric acid solution in presence of Uricase after (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min

**Figure 4.15** Absorption spectra of Ag nanoparticle solution (PVP, Mol wt. = 40kD) in presence of different concentration of uric acid, after 60 min: (a) 0 µM, (b) 10 µM, (c) 20 µM, (d) 30 µM, (e) 40 µM, (f) 50 µM. Inset: Linear plot of absorbance of Ag nanoparticle vs uric acid concentration (R\(^2\) = 0.9964), uric acid concentration range = 0 to 5 \times 10^{-5} \text{ mol.dm}^{-3}.

**Figure 4.16** TEM micrograph of Ag nanoparticles prepared using PVP of molecular weight 40kD (a) before addition of uric acid (b) after addition of uric acid

**Figure 4.17** AFM images of Ag nanoparticles prepared using PVP (Mol wt. = 40kD) (a) before addition of uric acid (b) after addition of uric acid
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Figure 4.19  Absorption spectra of Ag nanoparticle solution (PVP, Mol wt.= 160kD) in presence of different concentration of uric acid, after 60 min: (a) 0 µM, (b) 10 µM, (c) 20 µM, (d) 30 µM, (e) 40 µM, (f) 50 µM. Inset: Linear plot of absorbance of Ag nanoparticle vs uric acid concentration ($R^2=0.8826$), uric acid concentration range= 0 to $5\times10^{-5}$ mol.dm$^{-3}$.

Figure 4.20  Absorption spectra of Ag nanoparticle solution (PVP, Mol wt.= 160kD) in presence of different concentration of uric acid, after 8 hrs: (a) 0 µM, (b) 10 µM, (c) 20 µM, (d) 30 µM, (e) 40 µM, (f) 50 µM. Inset: Linear plot of absorbance of Ag nanoparticle vs uric acid concentration ($R^2=0.9679$), uric acid concentration range= 0 to $5\times10^{-5}$ mol.dm$^{-3}$.

Figure 5.1  Chemical structure of (a) Oligomer-Aliphatic urethane acrylate (AUA) (b) Reactive diluent-Trimethylolpropanetriacrylate (TMPTA) (c) Organic modifier for Cloisite 20A (where HT: hydrogenated Tallow) and (d) Organic modifier for Cloisite 30B (where T: Tallow)

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Figure 5.3  TEM image of Ag NPs embedded in AUA-TMPTA PNC film
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Figure 5.5  Plot of output fluence as a function of input fluence for 10 sec exposure duration

Figure 5.6  Variation of optical limiting property with exposure duration [(a) 1 sec vs (b) 1sec exposure duration]

Figure 5.7  Optical Limiting property of (a) control film and films with (b) Ag NPs (c) Thiophene/Ag NPs and (d) Cloisite 30B/Ag NPs as nanofillers

Figure 5.8  UV-visible transmittance spectra of PCN films containing Cloisite 20A as nanofiller (a) 0% (b) 2% (c) 5% (d) 10%.

Figure 5.9  FTIR spectra of PCN films (a) without nanoclay, (b) with 10% nanoclay (cloisite 20A)

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Figure 5.12  TEM images of PCN films containing 2% nanoclay (a) Cloisite 20A and (b) Cloisite 30B

Figure 5.13  SEM images of PCN films containing Cloisite 20A nanoclay (a) 0% (b) 2% (c) 5% (d) 10% and (e) 15%

Figure 5.14  DSC profiles of PCN films (a) without nanoclay (b) with 5%
Cloisite 20A and (c) 5% Cloisite 30B

**Figure 5.15** Pendulum hardness analysis of PCN films with different loadings of nanoclay (a) Cloisite 20A, (b) Cloisite 30B. (Inset: Gloss at 60° data for PCNs with different loadings of Cloisite 20A).

**Figure 5.16** TGA analysis of PCN films containing (a) 0% filler (b) 2% Cloisite 20A (c) 5% Cloisite 20A (d) 2% Cloisite 30B and (e) 5% Cloisite 30B. (Inset: Differential Thermogravimetric plots for PCN films containing (a) 0% filler (b) 2% Cloisite 20A (c) 5% Cloisite 20A (d) 2% Cloisite 30B and (e) 5% Cloisite 30B.)

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