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

5.1. Introduction

Inorganic-Organic hybrid nanocomposite materials have received great attention from the industrial community because of their wide range of novel physical properties. Relative to virgin polymer or conventional composites, polymer nanocomposites show significant improvement in certain material properties, such as barrier property, enhanced mechanical properties, optical limiting properties etc. In particular, metal nanoparticles based nanocomposite materials have found wide application in recent years as optical limiting materials. The widespread use of high power lasers operating over a wide range of wavelengths and pulse durations and the increase in the applications of lasers has led to a surge in the need for optical limiters, which are indispensable in the context of protection of optical components and the human eye from laser-induced damages. An ideal optical limiter is defined as a device which exhibits appreciable linear transmission below a threshold input fluence and a constant transmission above it [192]. Although numerous materials have been discovered and developed over the years as optical limiters, including materials such as phthalocyanines, porphyrins, fullerenes, carbon nanotubes, organic dyes etc. [193-198], metal nanoclusters based nanocomposites stand out as one of the best options owing to their unique nonlinear optical properties, such as two-photon absorption (TPA), saturable absorption (SA), reverse saturable absorption (RSA), and self-focusing/defocusing arising from nonlinear refraction [199-205]. Metal nanoparticles (NPs) dispersed in polymer matrices combine the properties of both the inorganic and polymer components, thereby yielding significantly enhanced performances [206]. The polymer matrix provides the platform for
maintaining the size, shape and dispersion of the metal nanoparticles- parameters which play a vital role in deciding the properties exhibited by the particles. At the same time the polymer matrix also provides additional qualities, such as processability, solubility or thermal stability to the system.

Another important application of polymer nanocomposite materials is in the field of flame retardants. Early flame retardants included use of halogenated compounds. But these are currently being phased out because of environmental concerns [207,208]. Alternatively, metal hydroxides [209-211] and intumescent flame retardant (IFR) [212,213] additives, as main halogen-free flame retardants (HFFR), have also attracted considerable attention. However, large loadings of IFR additives and metal hydroxides are usually needed (>60 wt %) in the polymer matrix to get high flame retardancy, which leads to significant loss in the mechanical properties of the polymer. Hence, layered silicates (clay)-polymer nanocomposites containing modified organophilic clay as nano fillers have been the focus of research over the past few years owing to their unique flame retardant properties [214-217].

The addition of clay to organic polymers differs from conventional blending of non-swellable inorganic fillers into polymers, as the clay nanofiller interacts with the organic matrix at a nano-scale level, and the final structure depends largely on the extent of intermixing and compatibility between the organic and the inorganic phases. Clay is identified as an inexpensive, environmentally benign nanofiller material with unique, mechanical, barrier and rheological properties. On adding just a tiny amount of clay to the polymer matrix, these new-generation composite materials exhibit significant decrease in the peak heat release rate (PHRR), change in the char structure, and decrease in the mass loss rate during combustion in the cone calorimeter [218-225]. It does not have the usual drawbacks associated with other fire retardant additives. Moreover, these PCN materials exhibit increased physical, thermal and mechanical properties [226-230].
Polyurethanes are the most widely used polymers in the field of polymer nanocomposites. The overwhelming popularity of polyurethane as the base matrix is due to its unique properties such as excellent abrasion resistance, flexibility, hardness, chemical resistance, solvent resistance, light stability and weatherability, and wide range of applications, including in the field of adhesives, foams, textiles, membranes, elastomers and rubber adhesion promoters, besides in coatings [231,232]. Inclusion of nanofillers into these polyurethane matrices leads to further enhancement in their thermal and mechanical properties, thereby expanding the scope of their application into more diverse fields. Hence, for all our applications polyurethane based oligomers were used as the base matrix.

Mechanical noncovalent blending, including melt blending and solution blending, is usually used for the fabrication of polymer composites. In case of metal nanoparticles based polymer composites, fabrication is mostly done by mixing preformed nanoparticles with the polymer in solution and casting the composite films (ex-situ). However, these methods put severe limitations on the homogeneous dispersion and interaction of the fillers with the base matrix. Therefore, in recent years focus has been shifted to the use of high energy radiation sources for engineering polymer nanocomposite materials. Compared to conventional techniques, the major advantages of using high energy radiation, including electron beam or gamma irradiation, for curing, are that these are pollution-free, high efficiency techniques that impart long service life, uniform cross-linking degree, and excellent heat-resistance and cold-resistance properties to the materials [233,234]. Moreover, inorganic/organic nanocomposites containing inorganic nanofillers fabricated using radiation curing method were found to exhibit distinctly enhanced properties compared to conventionally prepared materials [235]. In the case of metal-polymer nanocomposites, this technique facilitates in situ generation of metal nanoparticles in the polymer matrices [236,237]. Variation of parameters such as the radiation dose, dose rate and metal/polymer ratio allows easy control
over the size and dispersion of the metal nanoparticles as well as the overall properties of the nanocomposite material.

In this chapter, fabrication of flexible silver nanoparticles-polyurethane acrylate based polymer nanocomposite films (PNCs), possessing optical limiting properties, via electron beam irradiation route has been discussed. Aliphatic urethane acrylate was used as the base matrix. A 2Mev Electron beam source was used to achieve curing of the coating formulations by subjecting the samples to an optimized radiation dose. The PNC samples were characterized in detail and tested for their optical limiting properties using a Nd-YAG Laser operated at third harmonic wavelength of 355nm with 25ns pulse and 10 Hz cycle. The chapter also discusses the synthesis of modified montmorillonite clay based nanocomposite films using the same polymer matrix and study of their various properties including flame retardant property. A $^{60}$Co Gamma chamber was used to achieve curing of the coating formulations by subjecting the samples to an optimized radiation dose.

5.2. Fabrication of nanocomposite films

Radiation curing of polymers using ionizing radiation is an established technique for fabrication of polymer coatings and films. Therefore, this technique was adopted to fabricate uniform nanocomposite polymer films containing modified clay/insitu generated metal nanoparticles as nanofillers. Aliphatic urethane acrylate (AUA) was chosen as the base matrix (fig. 5.1a). Trimethylolpropane triacrylate (TMPTA) (fig. 5.1b) was used as the reactive diluent, which not only regulates the viscosity of the oligomer but also serves as a crosslinker by virtue of its three functional acrylate groups that help form connecting bridges between the polymer chains during the process of radiation induced curing of the oligomer.
5.2.1. Synthesis of Ag NPs/polyurethane acrylate based films

The precursor ion stock solution of silver nitrate was prepared in methanol as the solvent because of its ready miscibility with the oligomer-diluent reaction mixture. The AUA-TMPTA ratio was maintained at 4:1 to achieve optimum viscosity and to ensure maximum crosslinking between the polymeric chains. Three different volumes of Ag\(^{+}\) ion solution were added to 5g AUA-TMPTA mixtures to arrive at final Ag\(^{+}\) ion concentrations of 8, 15 and 30mM. Radiation doses were optimized at 150kGy to achieve non-tacky homogeneous polymeric films in which Ag NPs were generated in situ via radiolytic reduction of the precursor Ag\(^{+}\) ions.

5.2.2. Synthesis of organophilic clay/polyurethane acrylate based films

Cloisite 20A, a montmorillonite clay, modified with an organic modifier (fig 5.1c) and Cloisite 30B, a montmorillonite clay, modified with an organic modifier (fig 5.1d) were used as nanofillers to impart flame retardant properties to the polymer films. These modified montmorillonite clay samples in different concentrations (%w/w) were added to an optimized mixture (4:1) of AUA and TMPTA. To achieve uniform dispersion of the filler in the coating formulation, each of the samples was subjected to probe ultrasonication (Q700, Qsonica, USA) for 30 min. The formulations obtained were coated onto glass substrates and subjected to \(\gamma\)-radiation for a total absorbed dose of 150kGy to obtain non-tacky, homogeneous PCN thin films under aerated condition. The thickness of the EB cured coatings was found to be ~100\(\mu\)m as estimated by a thickness gauge ‘coat measure M12’ (Yuyutsu, JAPAN).
Fig. 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)

5.2.3. Characterization of Ag based films

The formation of Ag NPs in the polymer matrix was confirmed by the bright yellow colour generated in the film as compared to the colorless control polymer film. UV-visible spectroscopy of the films were carried out [fig 5.2] which show characteristic narrow Surface Plasmon Resonance (SPR) band of Ag NPs at ~420nm, thereby confirming the formation of more or less uniform sized, spherical silver nanoparticles within the polymer matrix. The intensity of the SPR band increased proportionately with increase in the Ag concentration of the PNC film.
Fig 5.2 UV-Vis spectra of PNCs containing (a) 8mM (b) 16mM and (c) 30mM Ag NPs as fillers.

Fig 5.3 presents the TEM image of the in situ generated Ag NPs. TEM analysis clearly indicated formation of uniformly dispersed spherical nanoparticles with average particle size of 6-8nm.

FE-SEM image shown in fig 5.4 also confirms the formation of uniform sized spherical Ag NPs embedded in the polymer matrix.
**Fig. 5.3** TEM image of Ag NPs embedded in AUA-TMPTA PNC film

**Fig. 5.4** FE-SEM image of Ag NPs embedded in AUA-TMPTA PNC film
5.2.4. Evaluation of Optical limiting property: proposed mechanism

The optical-limiting behaviors of the composites with different Ag NPs concentrations were measured using Nd:YAG laser with 25 ns pulse duration and 355 nm wavelength. The sample was mounted on a metal frame and the laser beam focused on the sample surface with a spot size of 1.0 mm diameter. The incident and transmitted energy were detected simultaneously by two power meters. The film was exposed to the laser beam for a duration of 10 seconds. The incident laser power was increased after every 10 second exposure till complete burnout of the samples was observed. The result is shown in Fig 5.5, which distinctly highlights the optical-limiting effect of PNC containing 30mM Ag NPs as the nanofiller. At very low output energy, the response of the composite was linear to the input energy. The linear transmittance was found to be approximately 82% while the limiting or threshold input fluence beyond which the sample stopped transmitting the laser beam was calculated to be 3.8 J/dm$^2$. Similar trends were observed for composites containing 8 and 16mM Ag NPs as filler. This clearly indicates that the transmittance and threshold fluence of the films was independent of the concentration of the nanofillers in the range under study; with the common base polymer matrix acting as the deciding factor in determining the extent of transmittance.

Although different processes such as transient absorption, two-photon or multi-photon absorptions, interband and intraband transitions and nonlinear scattering are known to lead to optical limiting behavior in metal nanoparticles, the predominant mechanism responsible for optical limiting behaviour in polymer films containing metal nanoparticles is Reverse Saturable Absorption (RSA). The RSA may be attributed to excitations from the plasmon band to the free carrier band of metal nanoparticles (eg. Ag NPs). At higher input fluences, fast decay of the free carriers to the plasmon band can also lead to optical limiting through Saturable Absorption (SA).
In order to study the effect of the exposure duration on the optical limiting effect of the PNC film, similar experiments were carried out by limiting the time of exposure to 1 second. Fig. 5.6 shows the variation in optical limiting characteristics for PNC containing 30mM Ag NPs with change in the time of exposure. Exposure for 1 second led to significant improvement in the optical limiting property of the material, which was manifested in the decrease in threshold fluence from 3.8 J/dm$^2$ to 1.2 J/dm$^2$. The dynamic range, which is defined as the ratio of the maximum input fluence till which material displays optical limiting behavior to the threshold fluence, was also found to increase from 22.34 to 80.10. In other words, exposure for lesser durations not only led to an early cut off for the laser transmission but also increased the overall lifetime of the material. This can be explained on the basis of the fact that continuous exposure for long durations led to accumulation of laser power within
a small area (determined by the beam diameter) thereby culminating in rapid degradation of the product.

In addition to Ag NPs as fillers, the effect of addition of fillers such as thiophene and modified montmorillonite clay (Cloisite 30B) in conjunction with Ag NPs, on the optical limiting behavior, was also studied. The results are highlighted in fig 5.7. It was observed that for an exposure duration of 1 second, change in the filler concentration or nature did not lead to any change in the threshold fluence of the materials. However, the presence of cloisite 30B as additional filler led to a slight increase in the initial output fluence of the materials. On the other hand Thiophene/Ag based films exhibited increased output fluence at higher input fluencies. At the same time, composites containing Cloisite 30B/Ag NPs as fillers showed early damage resulting in a narrower dynamic range compared to the other two composite films. Thus by simply adding an additional filler along with Ag NPs the optical limiting properties of the PNC films could be effectively tuned to get the desired output fluence or dynamic range without comprising on the threshold fluence of the material.

![Figure 5.6 Variation of optical limiting property with exposure duration](image)

**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

5.2.5. Characterization of clay based films

The characterization of Polymer Clay Nanocomposite (PCN) films was carried out by the following techniques

*UV-visible spectroscopy*

UV-visible spectrophotometry was employed to examine the transparency of the PCN films. Fig. 5.8 shows the UV-Visible spectra of the PCN films containing Cloisite 20A with ~100nm thickness. It was observed that the transparency of AUA-TMPTA films was slightly decreased with the incorporation of nanoclay filler. The transmittance of the PCN decreased marginally with the increase in the clay loading, particularly in higher range of visible light. The significant transparency of the PCN films supports the uniform dispersion of the clay in the polymer matrix. Similar trend was observed in case of films containing Cloisite30B nanoclay (data not shown).
**FTIR analysis**

The FTIR spectrum of control polyurethane acrylate film (Fig. 5.9a) exhibits the characteristic peaks of typical polyurethane acrylate: broad band at 3380 cm\(^{-1}\) (H-bonded NH stretching), 1735 cm\(^{-1}\) (C=O stretching), doublet at 2860–2930 cm\(^{-1}\) (stretching mode of -CH\(_2\)), 1462 cm\(^{-1}\) (bending mode of -CH\(_2\)), 1340 cm\(^{-1}\) (Stretching mode of CN), 1525 cm\(^{-1}\) for amide II (NH bending and CN stretching), 1242 cm\(^{-1}\) for amide III and 1033 cm\(^{-1}\) (C-O-C stretching). Fig. 5.9b presents the FTIR spectra of PCN films containing Cloisite 20A nanoclay. Signature of clay was clearly evident from the following IR peaks observed in the spectrum: a high intensity peak at 1042 cm\(^{-1}\) corresponding to Si-O-Si stretching modes and 890 cm\(^{-1}\) Al-OH-Al deformation of aluminates stretching modes associated with tetrahedral polyhedra [238].

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**Fig. 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)

XRD and SAXS analysis

XRD and SAXS analysis of the PCN films was performed in order to find out the dispersion of the nano-clay in the polymer matrix. Fig. 5.10(a) and 5.10(b) present the XRD data for PCNs with Cloisite 20A and Cloisite 30B, respectively. XRD data showed a significant shift in peaks position towards lower 2θ values in PCN films as compared to that of pure clay. Pristine Cloisite 20A and Cloisite 30B powder clay samples were found to have 2θ=3.36° (interlayer spacing=2.65nm) and 2θ=4.74° (interlayer spacing=1.88nm), respectively. The interlayer spacing between the silicate layers of clay increased when incorporated in the PCN matrices. The 2θ peak position of PCN-20A and PCN-30B nanocomposite samples shifted to 2.50° (interlayer spacing=3.5nm) and 2.92° (interlayer spacing=3.08nm), respectively. It was found that the PCN sample containing clay showed lower intensity peak as compared to pure clay sample. Moreover, the peak intensity was
found to decrease with the decrease in the clay concentration in the PCN films, suggesting the formation of mixed exfoliated/intercalated silicate nanolayers of the clay particles at lower clay loading. However, the decrease in $2\theta$ and corresponding increase in the interlayer spacing value for higher clay loading in PCN matrix also indicated significant intercalation of the layered structure of clay.

To determine the effect of temperature on the composite morphology, *in-situ* high temperature SAXS experiment was also carried out using PCN-20A-5% sample. In the first set of experiment, PCN sample was heated and scattering data was collected at different temperatures. It was observed that elevation in temperature above 100°C resulted in a shift of the peak towards higher $2\theta$ values, indicating a gradual decrease in the interlayer spacing of the silicate (Fig. 5.11a). This may be attributed to the elimination of water molecules trapped within the interlayer spacing of clay platelets, thereby causing a reverse delamination effect and restacking of the silicate layers.

In the second set of experiment, the PCN sample was subjected to an isothermal heating at 150°C for 50 min. The SAXS scattering data is shown in Fig. 5.11b. It was evident that no significant shift of the peaks occurs at 150°C till 50 min. Therefore, we subjected the PCN sample to a still higher temperature of 200°C for longer time period up to 315 min to see whether there is time and high temperature induced change in the intercalated/exfoliated structure of clay in PCN. However, in this case also, there was no significant shift in peak position observed (data not shown), which suggested that PCN is quite stable at higher temperature as far as intercalation/exfoliation of the clay in the PCN matrix is concerned.
**Fig. 5.10** X-ray diffraction patterns of (a) nanoclay powder-Cloisite 20A and PCNs containing 2% and 5% Cloisite 20A, (b) nanoclay powder-Cloisite 30B and PCNs containing 2% and 5% Cloisite 30B.

**Fig. 5.11** (a) SAXS diffraction patterns of PCNs containing 5% Cloisite 20A at temperatures (i) 25°C, (ii) 150°C and (iii) 200°C and (b) In-situ isothermal scattering data at 150°C as a function of time.
**TEM analysis**

Fig. 5.12a and 5.12b present the TEM images of PCN films containing 2% cloisite 20A and cloisite 30B nanoclays, respectively. The microstructure represents a well-ordered multilayer morphology consisting of alternate polymer and inorganic layers, although their interlayer spacing turns out to be much higher in the composite in comparison to the nanoclay powder samples. TEM micrographs highlight regions with uniform distribution and good dispersion of nanoclay particles in addition to the intercalated/exfoliated regions in the PCN matrix. This was also supported by XRD results showing higher interlayer spacing and lower intensity of the XRD peaks for PCNs compared to the neat nanoclay powder samples.

![TEM images of PCN films containing 2% nanoclay](image)

**Fig. 5.12** TEM images of PCN films containing 2% nanoclay (a) Cloisite 20A and (b) Cloisite 30B
SEM analysis

Fig. 5.13 presents the SEM images of the fractured surfaces of control polymer film and PCNs containing modified montmorillonite clay (cloisite 20A as representative clay nanofiller). Fig. 5.13a presents the SEM image of polymer film without nanoclay filler, and shows fairly homogenous bulk morphology which is smooth and dense and bears no evidence of pores or channels. This indicates a typical fractography feature of brittle fracture behavior, thus accounting for the low fracture toughness of the neat coating. In fig. 5.13b-5.13e, the grey colored regions indicate the bulk of the polymer matrix and the brighter regions indicate the distribution of clay particles. However, the phenomenon of exfoliation, intercalation and aggregation is difficult to study from SEM conclusively, which gets distinctly reflected in TEM micrographs and XRD studies. For clay loadings up to 5%, uniform dispersion of the silicate layers in the polymer matrix can be clearly observed. However, clay loadings of 10% and 15% were found to affect the overall morphology of the polymer matrix, manifested as an increase in the fracture surface roughness (Fig. 5.13d and 5.13e). An increase in fracture surface roughness is an indicator of crack deflection mechanism, which increases the absorbed energy of fracture by increasing the crack length during deformation [239].
Fig. 5.13 SEM images of PCN films containing Cloisite 20A nanoclay (a) 0% (b) 2% (c) 5% (d) 10% and (e) 15%
**DSC analysis**

The glass transition temperature $T_g$ of a polymer is an important indicator of its temperature/time dependent viscoelastic behavior, which is often an important factor in determining the usefulness of a given polymer. $T_g$ also provides information about inter/intra-molecular interaction between components of a polymer composite. In case of polyurethane-clay nanocomposites, changes in the glass transition temperature can be interpreted as a result of effective interaction between polymeric chains and the silicate surface. Fig. 5.14a, 5.14b and 5.14c present the DSC thermograms of AUA-TMPTA, PCNs containing 5% cloisite 20A and cloisite 30B nanoclays, respectively. Incorporation of the nano-clay was found to result in a minute shift in $T_g$ values of the composites towards higher temperatures. While $T_g$ for control film was found to be -2.76\(^{0}\), that for PCNs containing 5% 20A and 30B nanoclay were recorded to be 0.12\(^{0}\) and -0.93\(^{0}\) respectively, indicating reduced chain segment mobility induced by the modified clay [240]. This is probably due to the fact that the restricted relaxation behavior for the polymer nanocomposites with intercalated or exfoliated silicates primarily depends on the extent to which the layered silicates interact with the polymer matrix. Exfoliation would result in enhanced interaction culminating in a large shift in $T_g$ value. However, intercalation would lead to a relatively lesser degree of interaction, which gets manifested as only a marginal shift in $T_g$ values. This corroborates with the results obtained from SAXS analysis.
5.2.6. Property evaluation of PCN films

Pendulum hardness

Pendulum hardness is a qualitative test frequently used in coating in order to compare the surface hardness property of different coatings. As per standard test method (ASTM: D 4366-95) for pendulum hardness test of organic coatings, the ‘pendulum hardness’ of coatings is reported in terms of damping time (in seconds) of pendulum rested on the coating surface for a swing amplitude of pendulum to decrease from $12^0$ to $4^0$. This test method is based on the principle that amplitude of oscillation of the pendulum touching the coating surface decreases more rapidly on the softer coating because of higher degree of damping of oscillation. For a smooth surface, softer coating will exhibit lower damping time, whereas, harder coating will exhibit higher damping time. Results of pendulum hardness test performed on PCNs with varying concentrations of nanoclays, are presented in Fig. 5.15.

![DSC profiles of PCN films](image)

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

~ 115 ~
was observed that the incorporation of nano clay into AUA-TMPTA coating increased its pendulum hardness (i.e., damping time) up to 5% clay loading (cloisite 20A as well as cloisite 30B), beyond which, the pendulum hardness was found to decrease. Higher clay content (>5%) may have interfered with the crosslinking reaction between different polymer chains of the PCN matrix, resulting in a relatively softer surface, and thereby decreased pendulum hardness. It can be seen that as compared to Cloisite 20A, Cloisite 30B yielded better hardness in PCN film, which may be attributed to the better compatibility between AUA-TMPTA matrix and Cloisite 30B due to more polar modifier used in Cloisite 30B.

**Gloss at 60°**

Specular gloss of the cured samples was measured at 60° angle of reflectance using Novo triple angle Gloss meter (J402-268, Elcometer, UK) and the results are reported in gloss unit (GU). Specular gloss at 60° is a measure of the ability of coating surface to reflect a beam of light in a particular angle (i.e. 60°) without scattering. This is an important property of coating specially used for aesthetic and decorative purposes. The gloss values of gamma radiation cured PCN coatings with different loading of nanoclay cloisite 20A are presented in inset Figure 8. It was found that incorporation of nanoclay led to a decrease in the specular gloss with increasing nanoclay loading. Decrease in gloss of nanocomposites coating was attributed to matting effect caused by increase of surface roughness upon addition of the nanoclay.
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).

**Solvent resistance**

The PCN coatings prepared were also tested for their solvent resistance properties using acetone as a solvent. Lower the weight loss in acetone, better the solvent resistance property of the PCN film. 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 coating, above which the gel fraction was found to decrease gradually with the increase in filler loading (Table 5.1). Clay loading of 2% was observed to be the optimum value to achieve maximum extent of crosslinking in both cases. Expectedly, similar trend was found for the solvent resistance property of the PCNs in acetone (Table 5.1). This suggested that the presence of nanoclay influences the curing extent of the AUA-TMPTA polymer matrix; clay loadings up to 5%
facilitated the crosslinking of the polymer matrix, while filler loadings higher than 5% hindered the crosslinking process. These results were found to be in line with the hardness analysis results; higher crosslinking extent (gel fraction) of PCN films up to 5% clay loading led to harder coatings.

**Water uptake study**

One of the important factors affecting the acceptability of novel coating in engineering applications is the degradation of the coating in presence of moisture that will affect the physical and mechanical performances, thereby, leading to its failure. In case of PCNs with cloisite 20A as the filler, the % water uptake was found to be lesser than that in the control film for samples with clay loading up to 5%, whereas for clay loadings of 10% and 15%, the water uptake was found to be higher than that for the control (Table 5.1). The decrease in crosslinking of the polymer chains with increase in clay loading, as evident from the solvent resistance and gel fraction analysis data, is probably responsible for the increased water uptake shown at higher loadings. On the other hand, the decrease in water uptake at 2% and 5% loadings indicates that clay nano fillers at low concentrations can actually enhance the crosslinking extent of the polymer chains. However, in case of PCNs containing cloisite 30B as the filler, the water uptake was found to be higher than that for the control as well as PCNs with cloisite 20A for all filler loadings, which is attributed to the more hydrophilic nature of the modifier used in cloisite 30B.
Table 5.1 Water uptake (%), weight loss (%) in Acetone and Gel fraction of PCNs with different filler loadings

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<th>Water uptake (%)</th>
<th>Weight loss in acetone (%)</th>
<th>Gel fraction (%)</th>
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<td>2.23</td>
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<tr>
<td>PCN-30B-15%</td>
<td>11.12</td>
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TGA analysis: determination of flame retardency

Several mechanisms have been proposed to describe the flame retardant properties of PCNs. The general view of the flame retardant mechanism is that a carbonaceous silicate char builds up on the surface during burning, which creates a protective barrier to heat and mass transfer. The accumulation of layered silicates on the burning/gasifying sample surface is considered to be due to two possible modes. One is that the layered silicates are left on the sample surface as a result of the decomposition of the polymer matrix by pyrolysis. The other probable mode is the transportation of the layered silicates, pushed by numerous rising bubbles of degradation products and the associated convection flow in the melt, from the interior of the sample towards the surface. The nano-dispersed silicate layers thus slow down the decomposition rate and increase the temperature of degradation by acting as an excellent thermal insulator and mass transport barrier [241]. The flame retardancy of a material is
generally described in terms of its Limiting Oxygen Index (LOI), a parameter calculated from the char yield of the material using the Van Krevelen’s equation

\[
\text{LOI} = 17.5 + 0.4\sigma \\
\sigma = \text{char yield in } \% \text{ at } 850^\circ C
\]  \hspace{1cm} (1) [242]

An LOI value of 21 is normally considered as the threshold and materials exhibiting LOI values of 26 and higher are described as flame retardant materials [242]. In order to determine the thermal behavior and flame retardant properties of the polymer films, thermogravimetric analysis of the films was carried out. Fig. 5.16 presents the thermograms of PCN-30B and PCN-20A with clay loading of 2% (w/w) and 5% (w/w). The AUA-TMPTA coatings showed good thermal stability up to ~ 250°C. The thermal stability of the coatings showed marginal improvement upon incorporation of nanoclay [243,244]. However, the char yields of the films were found to increase significantly with increasing concentration of the clay nano-filler in the PCN film. The char yield values were correlated to the LOI values of the polymer coatings using equation 1. It was observed that an increase in clay loading resulted in a simultaneous increase in the LOI values of the samples (Table 5.2). The LOI values recorded were found to be higher than 21 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.
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.)

Table 5.2 Limiting Oxygen Indices (LOI) of PCNs with different filler loadings

<table>
<thead>
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<th>Clay Sample</th>
<th>LOI</th>
</tr>
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5.3. Conclusions

Polymer nanocomposite films containing predominantly in situ generated Ag nanoparticles and other nanofillers in trace quantities were successfully fabricated using E beam irradiation technique. TEM and FE-SEM analysis of the Ag nanoparticles based PNC films revealed formation of well dispersed, spherical nanoparticles in the polymer matrix. The optical limiting studies of the Ag containing PCN films yielded a threshold fluence of 3.8 J/dm² and a dynamic range of 22.34 for an exposure duration of 10 seconds, thereby indicating potential optical limiting applications. Similarly, transparent polymer nanocomposites reinforced with layered silicate inorganic fillers (modified montmorillonite clay) were successfully fabricated via environment benign-gamma radiation curing process. TEM and SEM analyses of the nanocomposites indicated well-dispersed organically modified nanoclay particles with a mixed intercalated/exfoliated structure, which was further supported by the XRD analysis data. In-situ high temperature SAXS study indicated that PCN films showed good stability up to 200°C as far as the intercalation/exfoliation of the nanoclay is concerned. The presence of nanoclay in the AUA-TMPTA matrix was found to influence the crosslinking extent of PCNs. The addition of nanoclay did not significantly change the thermal stability of the polymer matrix but was observed to hinder the burning process of the films. Also, it was found to alter the other properties of the PCN films, such as pendulum hardness, specular gloss at 60 degrees, water uptake and solvent resistance. The flame retardant property of the PCN coatings was evaluated in terms of Limiting Oxygen Index (LOI), which was found to increase with increasing clay loading and attained a maximum value of over 26 for 15% (w/w) clay loadings, thereby offering themselves as suitable candidates for potential flame retardant applications.