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Radiation Processing of Polymer-Based Nanocomposite

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Abstract. In this paper, the preparation of polymeric nanocomposite based on carbon nanotubes or/and graphene by radiation techniques were reviewed. The preparation of polyhedral poligomeric sisesquioxane (POSS)-polymer and montmorillonite-polymer nanocomposite using radiation methods were discussed. And the preparation of nano-particles/polymer nanocomposite s and polymer-polymer Nanocomposites via irradiation were also introduced.

Introduction

In general, the materials processing methods with the aid of physical effects, chemical effects and biology effects between high-energy radiation (such as gamma ray and electron beam) and matter is called radiation processing. At present, although the radiation processing obtain the very good application in many fields of polymwric materials[1-13], while the parathion of polymer-based nanocomposites via radiation technology is still a new field of polymer radiation processing.

Polymeric Nanocomposite Based on Carbon Nanotubes or/and Graphene

Carbon Nanotubes-Polymer Nanocomposites

Carbon nanotubes can be divided into single walled carbon nanotubes and multiwalled carbon nanotubes. The structure of carbon nanotubes is similar to that of the polymer, the mechanical properties and electrical properties of carbon nanotubes are excellent, which can be combined with the polymer to obtain high performance nanocomposites[14-19].

Tatro et al.[20] have irradiated poly(methyl methacrylate) (PMMA) and multi-walled nanotube (MWNT)/PMMA composites in air. The MWNT/PMMA composites were found to show increased radiation hardness with respect to the glass transition temperature and mechanical properties. The dielectric properties were changed more significantly for the composites than for neat PMMA. The results indicate that multi-walled nanotubes may enhance radiation hardness of mechanical properties in PMMA. Lee et al. [21] have prepared composites of single-wall, polyaniline and gold nanoparticles by a one pot synthesis using γ-radiation as source for initiation of polymerization and generation of Au nanoparticles. Karim et al.[22] also synthesized the composites of conducting polythiophene (PTh) with the host filler multi-walled carbon nanotubes (MWNT) by the *in situ* γ-radiation-induced chemical polymerization method at room temperature. The Characterizations of the molecular structure of the PTh-MWNT composites indicated that interfacial entrapment occurred between the MWNT and PTh; and the MWNT functioned as a template for PTh polymerization (Fig. 1).The conductivity through the PTh-MWNT composites was much higher than the value obtained for the bulk PTh powers synthesized by the same method. The PTh-MWNT composites showed thermogravimetric stability compared to the PTh homopolymer in the temperature range 0-800℃.

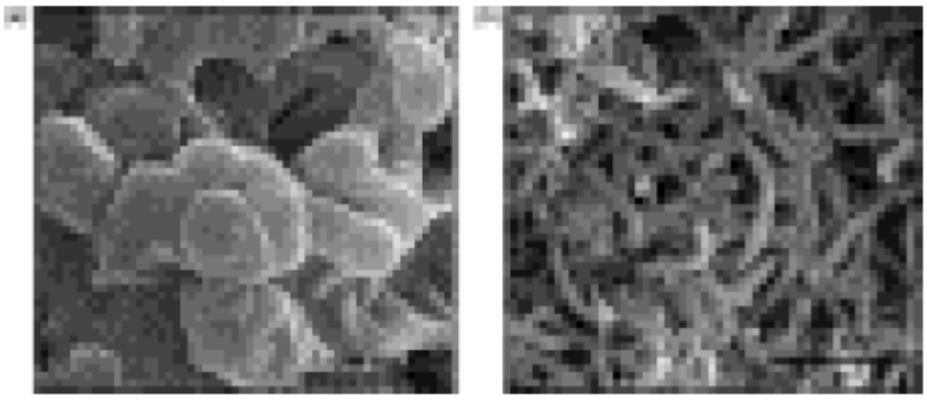

Fig. 1 SEM image of PTh-MWNT nanocomposites[22]

The carbon nanotube/polymer nanocomosites can be prepared by radiation curing method. Chen et al.[23] have MWCNT/epoxy resin (EP) nanocomposites by electron beam irradiation. The results showed that the surface of MWCNT access the small amount of containing, and disrupt the complete structure of the MWCNT after irradiation. When the irradiation dose of 170 kGy, grafted with the amount of oxygen groups most(about 4%) and the structural damage to a lesser extent. Compared with the original MWCNT/EP system, the MWCNT in EP dispersed more evenly after irradiation, and the maximum thermal decomposition temperature and glass transition temperature increased than that of the pure EP.

Li et al.[24] have also studied the γ-ray curing behavior of MWCNT/EP nanocomposites. The study found that the gel content of theγ-ray radiation curing composite system increased with increasing of radiation dose. Lu et al.[25] have also prepared the PVP-functionalized MWNT (PVP-MWNT)/epoxy resin composites by electron beam irradiation. It showed that the carbon nanotubes have PVP coating on the surface, and the PVP functional MWNT have good dispersion in the epoxy resin.

In addition, Dubey et al.[26] have prepared the ethylene vinyl acetate (EVA)/MWNT nanocomposites by melt mixing and subjected to different doses of γradiation. Theγradiation induced crosslinking was found to increase with MWNT fraction in EVA-MWNT nanocomposites. These results ruled out the possibility of a significant neutralization of single ionization spurs by MWNT addition. The incorporation of MWNT also resulted in increased hardness and higher density of the nano-composite matrix. Dubey et al.[27] have also investigated synergistic effect of MWNT induced reinforcement and high energy radiation induced crosslinking on the physic-mechanical and thermal characteristics of polychloroprene rubber (PCR)/ethylene-propylene diene rubber(EPDM)/MWNT elastomeric nanocomposites. In all the composites synergistic effect of radiation crosslinking and MWNT induced reinforcement were seen, suggesting radiation induced crosslinking between polymer and MWNT interface. Li et al.[28] have also prepared MWNT/polyethylene(PE) composites by γ-ray irradiation. The results showed that the volume resistivity at room temperature, the positive temperature coefficient (PTC) intensity of the MWNT/PE composites increased after radiation crosslinking.

Graphene/ Polymer Nanocomposites

Graphene is only a two-dimensional material with a carbon atom thickness. Graphene has a unique structure and excellent performance, which has great potential in improving the thermal properties, mechanical properties and electrical properties of the polymer[29-49].

Zhang et al.[50] have prepared polymer decorated graphene oxide by γ-ray induced graft polymerization. This approach presents a facile route for the preparation of dispersible GO and shows great potential in the preparation graphene –based composites by solution-processes. Ma et al.[51]also have synthesized graphene/carbon nanotubes (G/CNTs) hybrid fillers by γ-ray radiation reduction of graphene oxide (GO) in CNTs. And, have subsequently prepared poly(vinyl alcohol)

(PVA) composite films with enhanced mechanical properties and thermal stability by solution blending of G/CNTs with PVC matrix. The tensile strength and Young's modulus of PVA composite films containing 1 wt% G/CNTs were measured to be 81.9 MPa and 3.9 GPa respectively, which were 56% and 33.6% higher than those of pure PVA.

Lee et al.[52] have prepared graphene oxide/poly(acrylic)(GO/PAA) hybrid using a γ-ray pre-irradiation technique. The functional groups in graphene oxide were modified to peroxide in an O_2 environment with γ-ray radiation. Radical species from the thermal decomposition of peroxides initiated radical polymerization of the acrylic acid monomers. A genuine binary hybrid hydrogel of graphene oxide and PAA was obtained from a simple synthetic procedure based on γ-ray pre-irradiation without further additives.

POSS-Polymer Nanocomposites

Polyhedral oligomeric sisesquioxane (POSS) is composed of Si-O frame, and with a nanoscale three-dimensional structure of some organic groups, has the advantages of high melting point, low density, good dielectric properties. In preparation of POSS-polymer nanocomposites[53-64],the radiation method has become an important aspect of people's attention.

Choi et al.[65] have prepared polypropylene(PP)/POSS (PP/POSS) nanocomposites by in situ radiation-induced grafting of POSS onto PP. The mechanical property PP/POSS nanocomposites increased with the increase in POSS content and with the increase in absorption dose up to 5kGy, above which it started to decrease. The reduction of mechanical property at high doses can be attributed to the chain scission of PP by radiation. The degree of reduction in decomposition temperature of irradiated PP/POSS grafting POSS onto PP by radiation. Choi et al.[66] have also prepared POSS-reinforced polypropylene (PP) nanocomposites by a simple and economical radiation processing ,which has a great potential for the preparation of high-performance materials. The tensile strength of PP/POSS nanocomposites increased with an increasing POSS content up to 5 wt% and with an increasing absorption dose up to 50kGy. The tensile strength of irradiated PP/POSS nanocomposites decreased at high absorption dose due to the main chain scission of PP by radiation.The PP/POSS nanocomposites showed improved thermal stability due to the formation of crosslinked network brtween PP and POSS by radiation(Fig. 2).

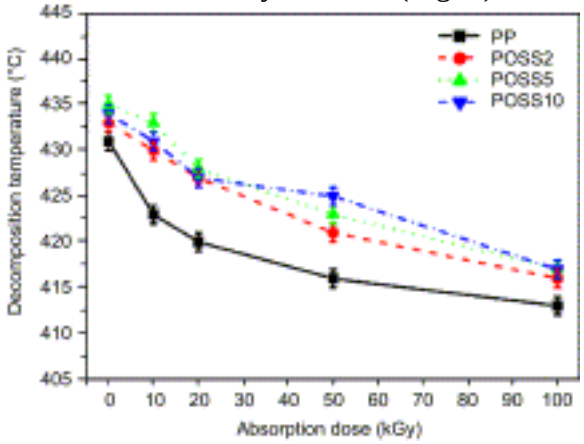

Fig. 2 Absorption dose on effect of decomposition temperature of PP/POSS nanocomposites[66]

Jung et al.[67] have prepared poly(lactic acid)(PL)/poly(ethylene glycol)-functionalized polyhedral oligomeric silsesquioxane (PEG-POSS) nanocomposites with or without triallyl isocyanurate (TAIC) by melt blending and electron beam irradiation , to enhance the flexibility. Based on the results of the crosslinking degree measurements, the PLA/PEG-POSS nanocomposites were crosslinked by electron beam irradiation in the presence of TAIC and their crosslinking degree reached up to 80% based on the absorbed dose and their compositions. And,the results showed that the crosslinked PLA/PEG-POSS nanocomposites wer homogenous without a micro-phase separation or radiation-induced morphological change. The PLA/PEG-POSS nanocomposites containing 15 wt% PEG-POSS exhibited the highest flexibility, and their tensile strength showed a

maximum value of 44.5 MPa after electron beam irradiation at an absorbed dose of 100kGy in the presence of TAIC, which is comparable to non-biodegradable polypropylene. The crosslinked PLA/PEG-POSS nanocomposites exhibited a higher thermal resistance above thei melting temperature in comparison to that of the neat PLA (Fig. 3), although their glass transition temperature was lower than that of the neat PLA. The PLA/PEG-POSS nanocomposites were biodegradable even though their biodegradability was deteriorated in comparison to that the neat PLA.

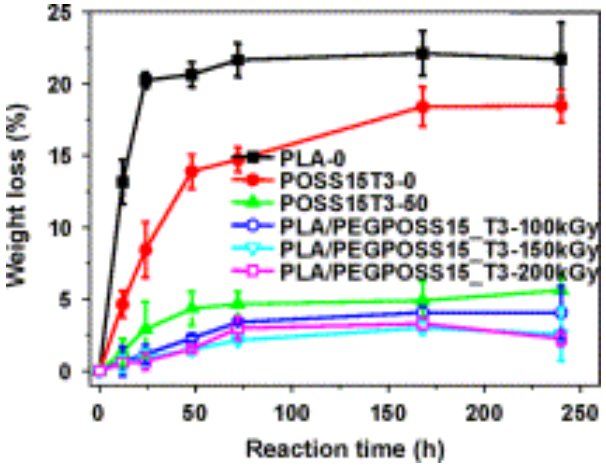

Fig. 3 Relationship between Reaction time and weight loss of PLA/PEG-POSS nanocomposites[67]

The POSS-polyurethane composites were prepared by using octavinyloctasilasesquioxane (OVS) and γ-ray irradiation. As an example, the POSS-polyurethane was prepared by using polycarbonate diol and liquefied 4,4`-diphenylmethane diisocyanate(Liquefied MDI). And, by γ-irradiation, radiation dose is 50kGy, irradiation dose rate for 10kGy / h. And, the sample 1 is unirradiated polyurethane prepolymer, the sample 2 is the radiation crosslinking polyurethane elastomer (without OVS), the sample 3 and sample 4 are the OVS-polyurethane radiation crosslinked samples (the adding quantity of OVS were 7% and 11%, respectively). Figure 4 is DMA charts of POSS-polyurethane. From Fig. 4 it can be seen that, prior to irradiation (sample 1) ,only one tagδpeak from the soft segment, which is mainly the contribution of the long chain of polycarbonate diol. After irradiation (sample 2), because theβ-HEMA polymerization and formation of polymeric chain segment, it appears a obvious tagδ peak due to poly(2-hydroxyethyl methacrylate) (PHEM) hard segment, and,the tagδ peak of soft segment shifts to higher temperature, which belonged to the confined effect of radiation crosslinking. After adding OVS, two tagδ peaks shift to more high temperature.This should be attributed to the contribution of OVS on radiation crosslinking polymerization[68,69].

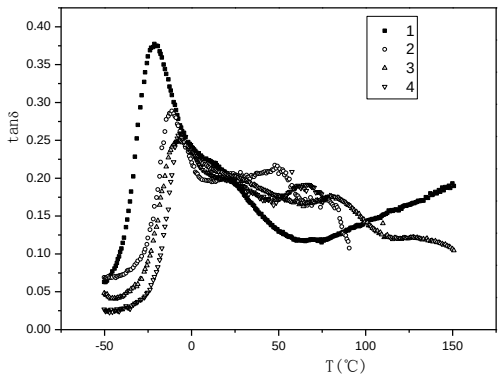

Fig. 4 DMA charts of radiation crosslinking polyurethane[68]

In adition, Preparation of POSS-polyurethane using radiation modificed polyols[70,71]. And, POSS is the use of OVS. More specifically, it is that preparing the POSS-filled modified polyol by OVS and gamma-ray irradiation, then POSS-filled modified polyols be used to preparation of POSS-polyurethane composites. For the preparation of POSS-filled modified polyol, OVS and polyols were mixed, and then get by gamma-ray irradiation. The sample 1(radiation modified polyaol, OVS (25wt) and polyether glycol (100wt)), the performance test results as shown in Table 1 The results show that, the POSS-polyurethane foam has the sound absorption performance and good heat resistance.

Tab. 1 Determination results of performance of POSS-polyurethane foam[71]

Properties	Determination results
Density(g/cm3)	0.045
Ope cell rate(%)	96.7
Average acoustic coefficient (125Hz-4000Hz)	0.42
Temperature of 5% weight loss(℃)	247.4
Temperature of 15% weight loss(℃)	290.5
Temperature of 50% weight loss(℃)	336.7

POSS-filled modified polyol can also prepared by adding of OVS and other vinyl monomers (methyl methacrylate (MMA), styrene (St) and acrylonitrile (AN)), then to preparing POSS modified polyurethane foam. Sample 2 (polyol (100wt), OVS (15wt), MMA (10wt)); sample 3 ((polyol (100wt),OVS (15wt), St (10wt)); samples 4((polyol (100wt),OVS (15wt), AN (10wt)). Performance test results of foaming material as shown in Table 2. The results show that, the POSS-polyurethane foam foams has the sound absorption performance and good heat resistance.

Tab. 2 Determination results of performance of POSS-polyurethane foam[71]

Properties	Determination results		
	Sample2	Sample3	Sample4
Density(g/cm^3)	0.053	0.052	0.045
Ope cell rate(%)	96.5	96.8	97.5
Average acoustic coefficient (125Hz-4000Hz)	0.41	0.36	0.37
Temperature of 5% weight loss(℃)	272.1	283.9	283.9
Temperature of 15% weight loss(℃)	295.2	296.2	298.4
Temperature of 50% weight loss(℃)	331.1	334.5	342.4

Montmorillonite-Polymer Nanocomposite

Montmorillonite is a kind of expandable layered inorganic compounds (layered silicate). And, polymer as object inserted between the layers, the lamellae expansion and lead to destruction of the lamellar structure, thus to nanoscale dispersion in the polymer matrix [72-84]. Misra et al.[85] have fabricated Polymer-clay nanocomposite (PCN) films by dispersing organically modified montmorillonite clay in varying concentrations of 2%,5%,10% and 15% (w/w) in an optimized composition of aliphatic urethane acrylate (AUA)- Trimethylolpropane triacrylate (TMPTA) mixture by ultra-sonication followed by ^{60}Co-gamma radiation induced curing. It showed that the gloss of the PCN films decreased, and fracture toughness and hardness of PCN films improved with

the incorporation of the clay in the PCN coatings. Dadbin et al.[86] have also prepared poly(lactic acid) (PLA)-layered silicate nanocomposite films by solved casting method.The films were irradiated with ^{60}Co radiation facility at dose of 30kGy.The tensile strength of the irradiated PLA films increased withadditin of 1 wt% triallyl cyanurate indicating crosslink formation. Significant ductile behavior was observed in the PLA nanocomposites containing pph of nanoclay.

Zhang et al.[87] have prepared polystyrene/montmorillonite nanocomposites by γ-ray radiation polymerization. The results showed that polystyrene (PS) could be easily inserted between the sheets of montmorillonite (MMT) to form intercalated nanocomposites. In these PS/MMT nanocomposites, the distance between the sheets of MMT was barely influenced by varying the content of the MMT.The glass-transition temperature of PS/MMT nanocomposites was obviously higher than that of the pure PS. Kundu et al.[88] have radiated a tube-like, naturally occurring halloysite clay mineral (HNTs) incorporated polyphosphazene (PPZ) elastomeric nanocomposites by electron beam. The efficiency of electron beam radiation over chemical initiation for intra and inter chain network formation within the resin was substantiated through oil and solvent resistance studies(Fig.5).

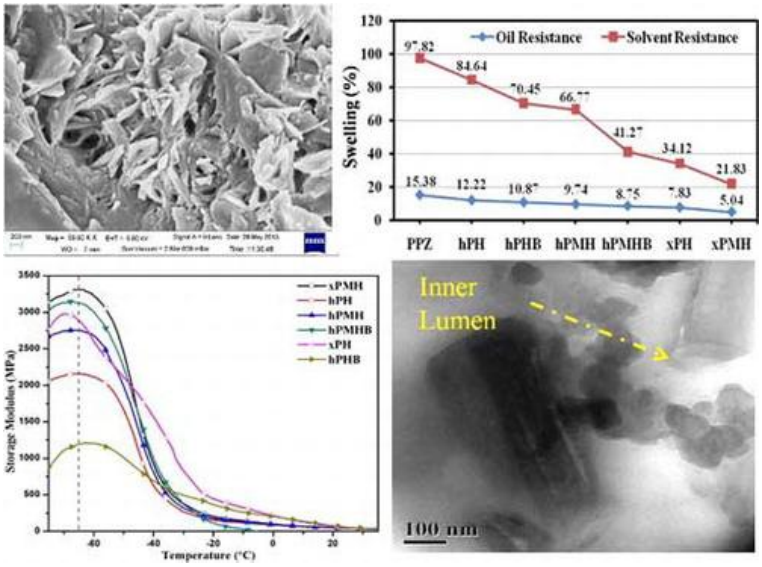

Fig. 5 Experimental results of PS/MMT nanocomposites[88]

Nano- particles/Polymer Nanocomposites

Gl äsel et al[89] have reported that through electron beam curing (EBC) of nanopowder/acrylate dispersion films the latter particles can impart ferroelectricity on thin polymeric nanocomposite foils which are of potential importance in piezo- and pyrosensorics. The CeSo nanoparticles, through high redox potential of the metal ions, can undergo pronounced radiation-induced solid-state polymerization. In radiation-cured polymeric nanocomposites the CeSo nanoparticles from crosslinks, thus efficiently modifying the viscoelastic properties. Cui et al. [90] have prepared organic-metal-salt(lead dimethacrylate ($Pb(MA)_2$)) nanofibers, and these $Pb(MA)_2$ monomeric nanofibers are successfully converted into PbS nanoparticles/polymer composite nanofibers through the combined use of γ-irradiated polymerization and gas/solid reaction (Fig.6). The resulting composite nanofibers have excellent thermal and chemical stability, and the PbS nanoparticles (with diameters of about 4 nm) are well dispersed in the polymer-fiber matrices. This approach could also be extended to metharylates containing other metal ions. This method would provide a platform for the fabrication of diverse and multifunctional polymer nanocomposite fibers, which would have potential applications in fabricating devices with optical, electric, and magnetic properties.

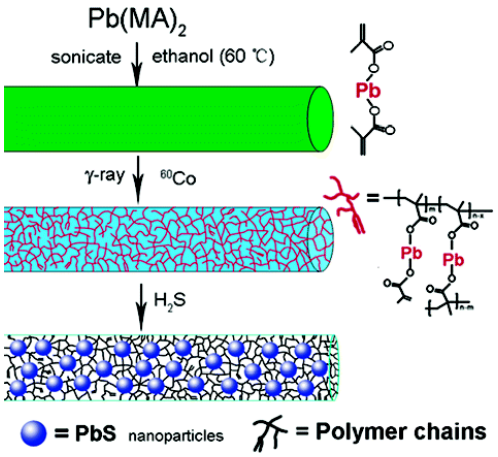

Fig. 6 Preparation of PbS nanoparticles/polymer composite nanofibers through the combined use of γ-irradiated polymerization and gas/solid reaction[90]

Liu et al.[91] have synthesized nanocomposites of stable nanosilver particles embedded in polyacrylonitrile matrix by γ-irradiation, in which the monomer acrylonitrile was polymerized and the silver ions were reduced simultaneously byγ-irradiation to form composites in situ. The strong interactions between silver ions with –CN groups of polyacrylonitrile are found. Karim et al.[92] have synthesized conducting polyaniline (PAN)-titanium dioxide (TiO_2) composite micron-sized rods using an in situ γ-ray radiation-induced chemical polymerization method. Aqueous mixtures of aniline, a free-radical oxidant and/or titania nanoparticles were irradiated withγ-rays. The formation of PAN- TiO_2 composite submicron-rods is the result of free aniline cation-radicals and adsorbed aniline cation-radicals on the surface of TiO_2 nanoparticles growing together with the aid of high-energy gamma irradiation. The results showed that the PAN-TiO_2 composite rods as having a diameter range of 0.2-0.5 μm, the composites have a higher degradation temperature than polyaniline alone.

In adition, Ali et al.[93] have also prepared films of poly(vinyl alcohol) / cadmium sulphide (PVA/CdS) nanocomposite containing various concentrations of Cd^{2+} ions using gamma radiation at different doses from 50 up to 200 kGy. The results showed that the CdS/PVA nanocomposites were dispersed as spherical CdS nanoparticles with homogeneity at either lower concentration of $CdCl_2$ or irradiation dose. The nano-rod structures of CdS was accompanied with small agglomeration at either higher $CdCl_2$ concentration or irradiation dose. A cubic phase and mixture of cubic and hexagonal phases of the prepared CdS nanoparticles were formed at lower and higher $CdCl_2$ concentrations, respectively.

Polymer-Polymer Nanocomposites

Literature data concerning the preparation of polymer-polymer nanocomposites via solvent crazing of polymers which is accompanied by polymer dispersion into fine (1-100 nm) aggregates composed of oriented molecules are analyzed. This phenomenon of solvent crazing is used for the preparation of nanoporous polymer matrices based on various amorphous and semicrystalline polymers. Introduction of a monomer into the nanoporous structure of the crazed polymer and its further in situ polymerization allow preparation of various polymer-polymer nanocomposites. These nanocomposites are characterized by specific mechanical, electric, and physicochemical characteristics. Applied aspects of the polymer-polymer composites prepared via solvent crazing are considered.

Robinette et al.[94] have synthesized polymer–polymer nanocomposites using radiation grafting techniques. It was found that 302MeV EB can be used to obtain controlled degrees of grafting by varying total dose and that such grafting is uniform throughout the thickness of the fiber mat. Procedures based on these techniques can be employed to generate polymer–polymer nanocomposites of dissimilar materials with geometric characteristics derived from the templating material.

Summary

In recent years, the radiation processing of polymer-based nanocomposites has got a great development as a new preparation method of polymeric nanocomposites. With the deepening of the understanding of radiation technology, radiation processing method will inevitably play a greater role in the preparation of polymer-based nanocomposites.

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