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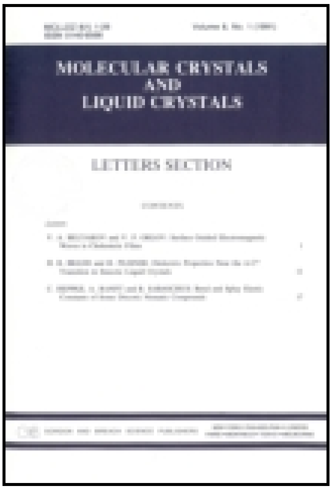

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Novel Poly(Propylene Carbonate) - Zinc Oxide Nanocomposites

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Published online: 17 Nov 2014.

To cite this article: Thi Nga Tran, Thanh Binh Mai, Long Giang Bach, Yeon Tae Jeong, Suman L. Jane & Kwon Taek Lim (2014) Synthesis and Characterization of Novel Poly(Propylene Carbonate) - Zinc Oxide Nanocomposites, Molecular Crystals and Liquid Crystals, 597:1, 45-51, DOI: 10.1080/15421406.2014.931789

To link to this article: http://dx.doi.org/10.1080/15421406.2014.931789

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Mol. Cryst. Liq. Cryst., Vol. 597: pp. 45–51, 2014
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.931789

Synthesis and Characterization of Novel Poly(Propylene Carbonate) - Zinc Oxide Nanocomposites

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A series of nanocomposites composed of poly(propylene carbonate)(PPC) and ZnO nanoparticles (NPs) were synthesized and characterized. Initially, (3-glycidyloxypropyl)trimethoxysilane was used to introduce epoxide groups onto the ZnO surface. Subsequently, the modified ZnO NPs were incorporated in PPC matrices by ring-opening copolymerization of epoxide groups on the surface of ZnO NPs and propylene oxide with carbon dioxide. The structures of the modified ZnO NPs and nanocomposites were confirmed by fourier transformed infrared spectrometry analysis. The morphology of the nanocomposites was investigated by scanning electron microscopy and transmission electron microscopy, where ZnO NPs were well dispersed in the polymer matrix. The thermogravimetric analysis study showed that the nanocomposites exhibited remarkable increasing in thermal property compared to the neat polymer.

Keywords Poly(propylene carbonate); zinc oxide; carbon dioxide; thermal property; biodegradable polymer.

1. Introduction

Poly(propylene carbonate) (PPC), a biodegradable and biocompatible aliphatic polycarbonate composed of carbon dioxide (CO_2) has attracted extensive attentions with a potentially wide range of applications [1, 2]. The incorporation of CO_2 into a polymer is an efficient route to reduce CO_2 greenhouse gas pollution, "white pollution", and overcome shortages in petroleum [3–5]. However, the poor thermal stability and relatively low mechanical property of PPC has limited its applications [6, 7]. Therefore, great efforts have been devoted to improve the deficient thermal and mechanical property of PPC. Among them, the fabrication of nano-filler/PPC composites is commercially advantageous because the physical properties are readily manipulated by the type and concentration of fillers. However, the

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high loading level of fillers leads to the poor dispersion of the nanoparticles into the polymer matrix, which leads to the deterioration of polymer properties [2, 7, 8]. Therefore, it is still a challenge to obtain superior properties of PPC composites with sustained composition and uniform dispersion of nano-fillers [3, 4, 8, 9]. Zinc oxide (ZnO) in nanoscale has attracted increasing attentions as a promising material for multifunctional organic-inorganic nanocomposites in view of its outstanding properties, including excellent optical, electrical, and antimicrobial properties. It is abundant in nature and environmentally friendly having high chemical stability, good thermal stability and high mechanical rigidity [2, 8, 10, 11].

Herein, a novel composite material composed of ZnO NPs covalently embedded into PPC has been disclosed. It was found that the loading of ZnO NPs into the polymer matrix by covalent bonds has caused a significant improvement of thermal properties compare to the neat polymer.

2. Experimental Details

2.1. Materials

PO, (3-glycidyloxypropyl)trimethoxysilane (GPTS) and ZnO NPs were purchased from Sigma Aldrich. PO was purified by vacuum distillation with calcium hydride. The double metal cyanide (DMC) catalyst was synthesized according to the literature [5]. CO_2 (99.99%) was passed through a column of molecular sieve $4A^0$ prior to the polymerization. All other chemicals were purchased from commercial sources and used without further purification.

2.2. Surface Modification of ZnO NPs

The ZnO NPs were introduced into a flask containing GPTS and isopropyl alcohol (IPA). The mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. After reaction, the product were thoroughly washed with IPA by several centrifugation-redispersion cycles to remove unreacted GPTS and then dried in a vacuum oven until constant weight, to yield ZnO epoxy-functional NPs (ZnO-EO) with the grafting density of 6.82% as determined by TGA.

2.3. Preparation of ZnO-PPC Nanocomposites

A certain amount of ZnO-EO, PO and DMC catalyst (Table 1) were quickly introduced into an autoclave reactor. The autoclave was sealed and pressurized by injecting CO_2. The temperature was increased to a desired value to start the polymerization. After 24 h, the autoclave was cooled down to room temperature, followed by slow releasing of unreacted CO_2 and PO. The product was dissolved in dichloromethane, then treated with a 10% NH_3 solution for removal of the catalyst, and dried under vacuum at 40°C. The same procedure was carried out for synthesis of pure PPC.

2.4. Characterization and Measurements

The fourier transformed infrared spectrometry (FT-IR) was measured with a BOMEM Hartman & Braun FTIR spectrometer. Scanning electron microscopy (SEM) analyses were carried out by using a field emission scanning electron microscopy (FE–SEM)

Table 1. The composition, char yards and T_d (at 20% and 40% weight loss rate) of PPC and ZnO-PPCs [a].

Entry	Sample	ZnO wt% Feeding (%)	ZnO wt% TGA (%)	$T_d^{20\%}$ (°C)	$T_d^{40\%}$ (°C)	Char Yards at 700°C (%)	Major Total Weight Loss (%)
1	**ZnO-EO**	—	—	—	—	92.06	6.82
2	**PPC**	—	—	209	218	0.37	95.41
3	**ZnO-PPC1**	20	19.74	246	257	19.74	76.41
4	**ZnO-PPC2**	30	29.95	271	287	29.95	67.38
5	**ZnO-PPC3**	40	39.82	312	331	39.82	57.44
6	**ZnO-PPC4**	40	39.01	301	323	39.01	58.18
7	**ZnO-PPC5**	50	49.48	337	392	49.48	47.57
8	**ZnO-PPC6**[b]	50	48.91	328	387	48.91	48.42

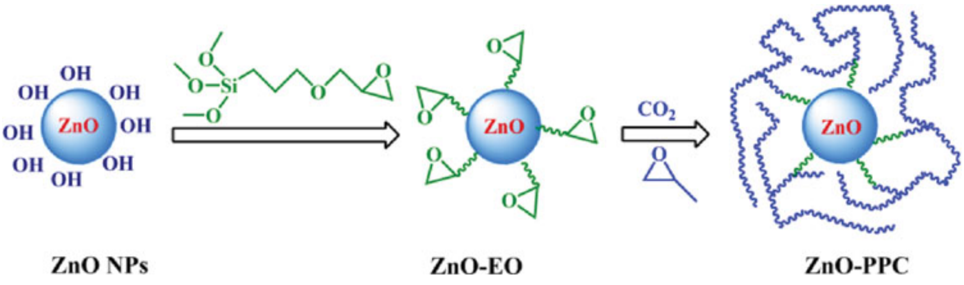
[a] Polymerization condition: $v_{PO} = 5.00$ mL, [catalyst] = 1% mol, $p_{CO2} = 50$ bar, temp = 100 °C, time = 24 h.

[b] Temp = 80 °C

(HitachiJEOL-JSM-6700F system, Japan). Transmission electron microscopy (TEM) images were recorded using a Joel JEM 2010 instrument (Japan). Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 analyzer (USA).

3. Results and Discussion

The synthetic approach for the preparation of nanocomposites was illustrated in Scheme 1. The ZnO-PPC nanocomposites were prepared by a grafting-through approach by the copolymerization of ZnO-EO and PO with CO_2.



Scheme 1. The synthetic route for the preparation of ZnO-PPC nanocomposites.

3.1. *Structural Characterization*

Figure 1 showed typical FT-IR spectra of the ZnO NPs, ZnO-EO, pure PPC and ZnO-PPC nanocomposites. The absorption bands of ZnO were clearly identified with a strong peak around 497 cm^{-1}, which is indicative of two transverse optical stretching modes of ZnO [3, 7]. Additionally, the broad absorption band at 3409 cm^{-1} is ascribed to the O–H vibration on the ZnO NP surface [4]. For the ZnO-EO spectrum, the characteristic stretching vibration peaks of –Si-OH and Si–O–Si were observed at 883 cm^{-1} and 1081 cm^{-1},

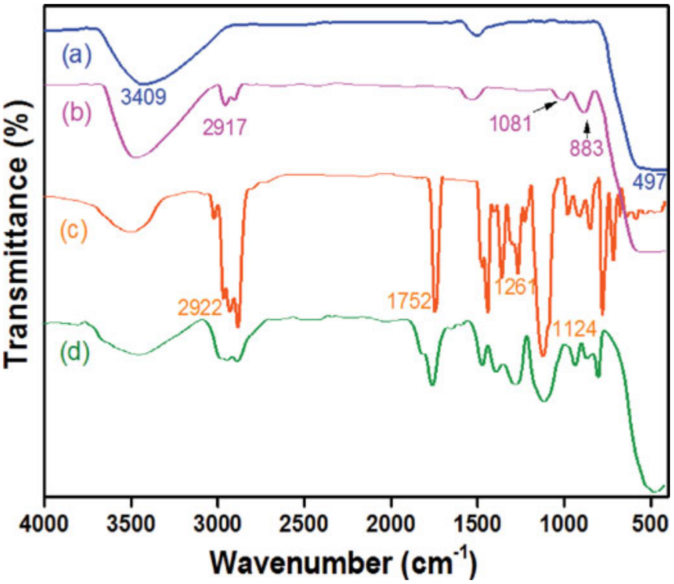


Figure 1. FT-IR spectra of ZnO NPs (a), ZnO-EO (b), PPC (c) and ZnO-PPC (d).

respectively [5, 6]. Additionally, the appearance of the saturated C–H absorption bands at 2917 cm^{-1} could be inspected [9]. Figure 1c showed the typical FT-IR spectrum of pure PPC. Three characteristic peaks at around 1752, 1124 and 2922 cm^{-1} which were corresponded to the stretching vibration of carbonyl groups (C=O), ether linkage (C–O–C) and alkyl groups (C–H), respectively, should be noticed. Upon the modification by ring-opening polymerization, all these characteristic peaks of PPC were well detected in the spectrum of ZnO-PPC nanocomposites, suggesting the formation of PPC grafted on the ZnO NP surface.

3.2. Morphology Characterization

The surface morphology of representative ZnO-PPC nanocomposites was investigated by SEM as shown in Figure 2a and b. Compared to pristine ZnO (Fig. 2a), it can be observed that there was the formation of the polymer layer on the surface of ZnO NPs (Fig. 2b) with almost uniform thickness upon the polymerization. Moreover, TEM images also provide additional information regarding the nanostructure of the pristine ZnO (Fig. 2c) and ZnO-PPC nanohybrids (Fig. 2d). Upon the surface engineering of ZnO with PPC, it was expected that the aggregation of the NPs could be diminished and their colloidal stability in organic solvents could be dramatically enhanced. The TEM samples were prepared by drop-casting of nanoparticles dispersed in chloroform onto carbon coated carbon grids. By comparing TEM images of pristine ZnO in Figure 2c and the nanocomposites in Figure 2d, it was worthy to notice that the agglomeration propensity of ZnO NPs was remarkably reduced upon covalent grafting of PPC. In addition, the high resolution (HR) TEM images of the nanocomposites (inset of Fig 2d) revealed that the darker contrast inner core of ZnO nanoparticles was wrapped with the lighter contrast outer shell of polymers. The thickness of the polymer layer is estimated to be around 10 nm from the HR-TEM images.

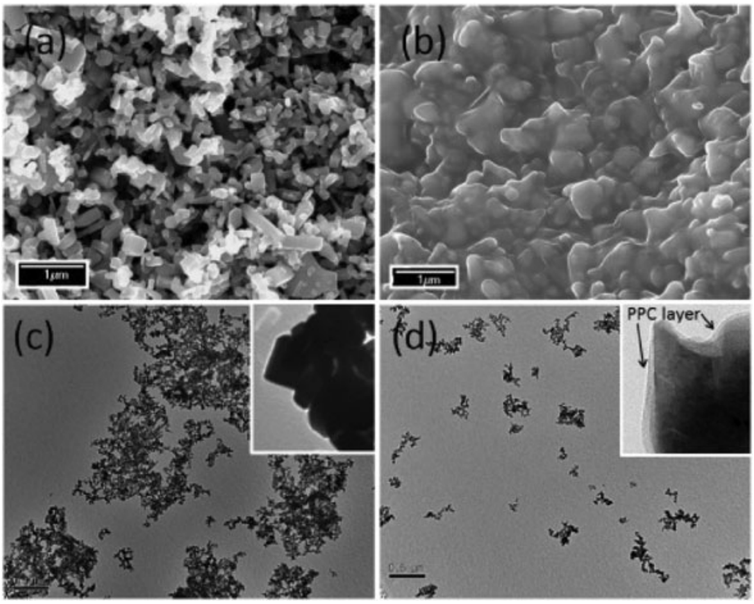


Figure 2. SEM and TEM images of ZnO NPs (a, c) and ZnO-PPC (b, d), respectively.

3.3. *Thermal Property*

TGA was performed to investigate the effect of ZnO on the thermal stability of the PPC matrix. Figure 3 shows TGA curves of PPC, ZnO-EO and a systematic series of ZnO-PPC nanocomposites. The TGA curve of pure PPC shows the major weight loss region at around 200–280°C, which is due to the degradation of the polymer. The ZnO-PPC nanocomposites

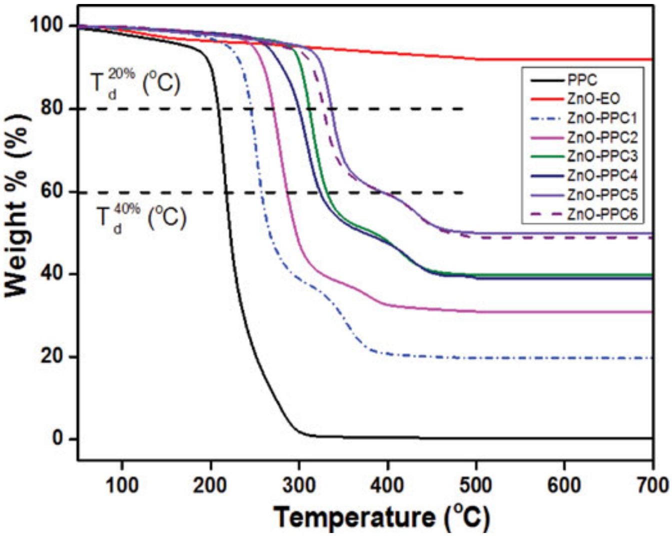


Figure 3. TGA thermograms of PPC, ZnO-EO and a series of ZnO-PPC nanocomposites.

initiate major decomposition at the temperature range of 270–450°C. The total weight loss at this stage is corresponding to the surface grafted PPC on the ZnO surface (Table 1). Impressively, the ZnO-PPCs exhibit a higher decomposition temperature (T_d) than that of PPC. Table 1 shows the composition, char yards and T_d (at 20% and 40% weight loss rate) of the polymer and nanocomposites. It is observed that the polymer lost 20% of weight at the T_d of 209°C, on the contrary nanocomposites lost the same weight at the higher T_d. The analogous circumstance was obtained at $T_d^{40\%}$. The shift of T_d to higher temperatures suggests that the thermal property of PPC can be manipulated by covalent incorporation of ZnO NPs. The phenomenon could be attributed to the protecting effect of ZnO NPs against the oxygen attack, providing sufficient resistant surface and network to the PPC matrix [11, 12]. Furthermore, the thermal property of ZnO-PPCs was improved in response with the increase of the ZnO content. Inversely, the opposite phenomenon was recorded in the case of decreasing the polymerization temperature with the same feeding reactants amount (entry 5&6, 7&8), which could be deduced by the effect of the PPC molecular weight [1, 4]. All the nanocomposite samples showed remarkably higher T_d than PPC itself, indicating that the thermal stability of PPC was substantially improved by incorporation of ZnO NPs. This thermal stability improvement was considered to covalent bonding between PPC and ZnO, which weakened the random main chain thermal scission, as well as chain unzipping reaction, of PPC [1, 3].

4. Conclusions

The ZnO-PPC nanocomposites were prepared *via* a grafting-through approach by copolymerization of functional ZnO-EO NPs with PO and CO_2. The covalent anchoring of PPC onto ZnO NPs was confirmed by FT-IR. The SEM and TEM images of PPC nanocomposites suggested the uniform dispersion of ZnO NPs in the PPC matrix. The thermal property of PPC was enhanced remarkably upon the covalent bonding of ZnO and PPC. Moreover, the thermal stability of the nanocomposites was found to be controllable by adjusting of polymerization conditions.

Acknowledgments

This work was financially supported by the Joint Program of Cooperation in Science and Technology through NRF grant funded by the MEST (No. 2011-0025680).

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