Modification of polypropylene carbonate *via* PDAH melt end-capping and GNP incorporation

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Abstract

Carbon dioxide, CO_2, is a molecule that has recently developed a high public profile. Knowledge about possible forms of carbon sequestration and utilization of waste CO_2 as an environmentally benign feedstock to produce useful materials is attracting industrial interest. One option is synthesizing copolymers from carbon dioxide and epoxides, which are one type of polyalkylene carbonate (PAC). Such copolymers, for example, poly(propylene carbonate) (PPC), were first reported by Inoue in the late 60s, and have recently been increasingly studied. Unfortunately, the performance of PPC is limited by its poor thermal stability, low heat deflection temperature (HDT), which is limited by its amorphous character, and low glass transition temperature, T_g. Therefore increasing the thermal stability to improve the processing performance and increasing the T_g and HDT are common targets for the polymer technologist working in the field of PPC based materials.[1;2]

In our unpublished work, we have found that melt compounding PPC with pyromellitic dianhydride (PDAH), namely a tetra-carboxylic aromatic dianhydride, acting as end-capping agent and chain extender, in addition to increasing the thermal stability, it contributed to the preservation of molecular weight during melt extrusion, and enhanced the stiffness. Herein, we addressed graphite nanoplatelets (GNP) incorporation into PDAH modified PPC (PPCPA) (PPC: Qpac40 from Empower materials, USA) as a novel approach to improve the properties of PPC. The effect on the polymer properties of various grades (Table1) and loadings of GNPs in melt compounding using a bench scale double screw extruder was be studied. A major focus was on the thermal properties and stiffness of modified PPC upon the addition of GNP.

The dispersion and filler polymer interactions were studied by rheology frequency sweeps. The tan δ trends at low frequency revealed the establishment of the first rheological percolation threshold from 4 wt% GNP and the main threshold from 10 wt% GNP [3]. Also, the dependence of the G' slope at high frequencies in some samples suggested the occurrence of tethering of the polymer chains from the filler surfaces[4]. The rheological main percolation thresholds occurring at levels of filler higher than 10 wt%, were general indicators of particle agglomeration in the studied compounds [3]. Large aspect ratio agglomerates and particles with thickness in the micro and nanoscale are observed in the SEM images (Fig. 1). The interphase of the fracture surfaces reflected various levels of filler-polymer interaction and modification degree of the interphase which were dependent on the filler grade.

The thermal stability was in great extent improved by the PDAH modification; however the GNPs had a significant contribution mostly depending on the loading and filler acidity. When the loading was increased $T|_{ons(i)}$ also increased as a sign of the mitigation of random chain scission [1,2]. In contrast, in particular when the filler acidity was high, the $T|_{5\%}$ was decreased, also an additional onset appeared (ons(ii)) as the result of increased chain unzipping catalyzed by the acid residues (Table 2). Mechanical reinforcement was observed in all cases once the secondary rheological threshold was achieved, approximately from a level of 6 wt% GNP, and was accompanied by a T_g increase. With increased loading, stiffening clearly took place in the case of GNP2 and GNP3 fillers, in contrast to GNP1, where the opposite was seen. This latter case is attributable to polymer degradation caused by the acid residues in the filler. ***At 15 wt% GNP2, increases of 10°C in T_g and 300 / 3000 % in E' were measured at 20 /30 °C, respectively (Fig. 2)***. The thermal stability and stiffness were mainly modified by the filler loading and the acid residues in the GNP and were mostly independent on the filler morphology.

References

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Figures

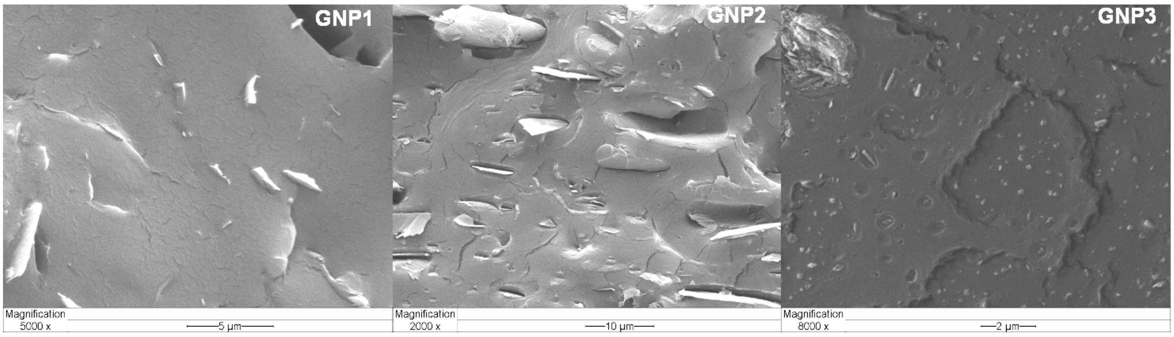

Fig. 1 SEM images from fracture surfaces of composite samples with 3 wt% filler

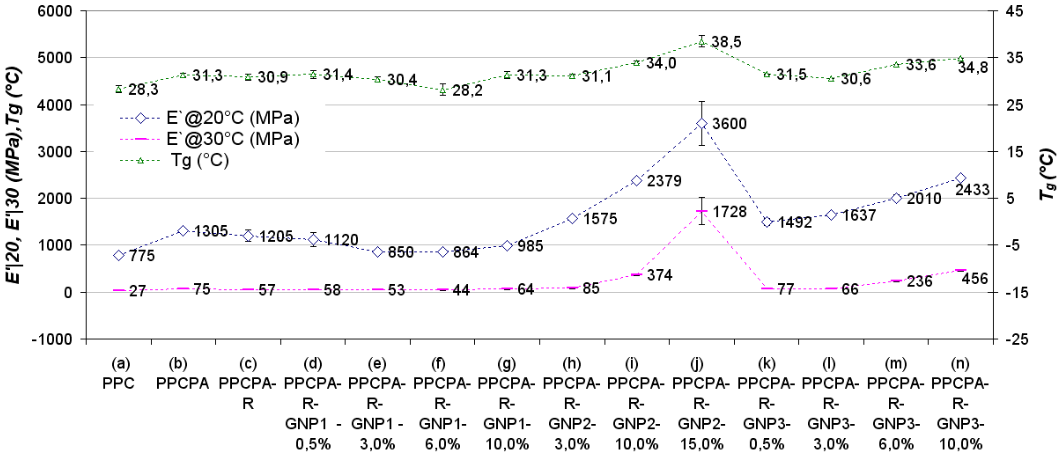

Fig. 2 DMTA characterization parameters: storage modulus at 20 and 30°C and glass transition temperature ($E'|_{20}$, $E'|_{30}$, T_g) for unfilled and GNP-PPCMA composites.

Tables

Table 1. GNP characteristics supplied by XG Sciences (producer) and measured at lab***

Abbr.	Grade	Surface area (m^2/g)*	Avg. thickness (nm)*	Avg. diameter (µm)*	Carbon content (wt%)*	Acidity (MgNaOH/g GNP)**
GNP 1	xGNP M15	150	6	15	99.5	7.2
GNP 2	xGNP M25	120	6	25		1.9
GNP 3	xGNP C500	500	2	<2		0.2

Table 2. TGA parameters for unfilled and GNP-PPCPA composites

Sample index	Sample Name	Filler Grade	$T|_{5\%}$* (°C)	$T|_{Ons(ii)}$* (°C)	$T|_{Ons(i)}$* (°C)	$Res|_{400}$* (wt%)
a	PPC	-	229	-	242	0
b	PPCPA	-	255	-	263	0.1
c	PPCPA-R	-	255	-	263	0.2
d	PPCPA-GNP1-0.5%	GNP 1	257	-	278	0.4
e	PPCPA-GNP1-3.0%	GNP 1	229	211	285	2.6
g	PPCPA-GNP1-10.0%	GNP 1	185	186	280	9.5
h	PPCPA-GNP2-3.0%	GNP 2	261	-	282	2.4
i	PPCPA-GNP2-10.0%	GNP 2	254	-	290	9.8
j	PPCPA-GNP2-15.0%	GNP 2	254	-	289	14.5
k	PPCPA-GNP3-0.5%	GNP 3	263	-	277	0.6
l	PPCPA-GNP3-3.0%	GNP 3	262	-	280	2.6
n	PPCPA-GNP3-10.0%	GNP 3	259	-	283	9.8

**Parameters from TGA 10°C/min in N_2: $T|_{5\%}$: Temperature at 5 wt% loss, $T|_{Ons\ ii}$: onset of the secondary degradation stage, $T|_{Ons\ i}$: onset of the main degradation stage, $Res|_{400}$: residue at 400°C.*