Imidazolium Salts as Liquid Coupling Agents for the Preparation of Polypropylene-Silica Composites

Ricardo K. Donato,[1] Moisés A. Benvegnú,[1] Luciano G. Furlan,[2]
Raquel S. Mauler,[2] Henri S. Schrekker[1]

[1]*Laboratory of Technological Processes and Catalysis, Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, CEP 91501-970, Porto Alegre, RS, Brazil*
[2]*Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, CEP 91501-970, Porto Alegre, RS, Brazil*

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ABSTRACT: This article describes the application of ionic liquid 1-decyl-3-methylimidazolium tetrafluoroborate in the preparation of polypropylene-silica composites. The sol-gel technology was used to prepare xerogel silica-ionic liquid hybrid **S1**, which was obtained as a free flowing powder of aggregated spherical particles. Ionic liquid free silica **S2** was obtained by extraction and calcination of **S1**. Melt blending of isotactic polypropylene with **S1** and **S2** afforded the composites **C1** (with ionic liquid) and **C2** (without ionic liquid), respectively. The presence of ionic liquid on the **S1** silica surface promoted significantly improved silica dispersion in the polymer matrix and prevented compression of the silica particles. Furthermore, the crystallization temperature of composite **C1** was significantly higher, which indicated that silica-ionic liquid filler **S1** acted as nucleating agent. The resistance to thermal decomposition of both composites was increased, but this was higher in the presence of ionic liquid. These results show that liquid salts can function as coupling agents and compatibalizers for the preparation of polymeric composites with differentiated properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 304–307, 2010

Key words: compatibilization; additives; thermal properties; polyolefin composites; interfaces

INTRODUCTION

Nanocomposites of organic polymers and inorganic nanoscale building blocks have attracted intensive academic and industrial interest.[1] The small size of the inorganic filler of polymeric nanocomposites results in a dramatic increase in interfacial area, which distinguishes this class of materials from traditional composites. This property allows the preparation of polymeric nanocomposites with advanced properties using lower contents of inorganic filler. However, one of the most important criteria to achieve these properties is a high degree of filler dispersion in the polymer matrix. In general, this is difficult to obtain with inorganic fillers due to the presence of hydrogen bonds between the filler particles, which promotes aggregation. When these inorganic fillers are applied in apolar polymer matrices this problem is even more severe as a result of the weak interaction between the apolar matrix and the polar filler. Principally three strategies are applied to increase this interaction: (1) Functionalization of the polymer surface with polar groups, (2) modification of the polar filler surface with apolar groups, and (3) application of an interfacial modifier or compatibalizer.

Nanoscale inorganic fillers are classified in three principal classes by their geometry, including particulated, lamellar, and fibrous materials.[2] Various reasons make silicas an attractive source as inorganic nanofillers for the preparation of polymeric nanocomposites.[3] It is a cheap source, which can improve the physicochemical properties of the polymer matrices. However, a drawback is its strong tendency to aggregate into larger silica agglomerates. Lately, we reported about the preparation of xerogel silica's with highly distinct morphologies in the presence of imidazolium ionic liquids (ILs).[4,5] Herein we report about the preparation of an *in situ* modified xerogel silica with IL 1-decyl-3-methylimidazolium tetrafluoroborate as morphology controller. The IL supported on the silica surface functioned as coupling agent in the melt blending process with polypropylene (Fig. 1) and promoted a higher degree of silica dispersion in the corresponding polymeric composite.

EXPERIMENTAL

A highly isotactic polypropylene (iPP) (trade name H-503, MFI = 3.5 g/10 min, M_w = 470.000 g/mol) provided by Braskem S.A. (Triunfo, Brazil) was used

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Correspondence to: H. S. Schrekker (henri.schrekker@urgs.br).

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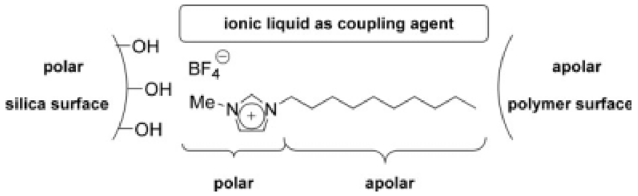

Figure 1 Generalized representation of the IL function as coupling agent in the formation of polymeric composites.

in this study. A procedure reported previously in the literature was used for the synthesis of 1-decyl-3-methylimidazolium tetrafluoroborate and the spectral data were in accordance with the literature data.[6] Tetraethoxysilane (TEOS) was used as purchased from Sigma-Aldrich and aqueous HF was used as purchased from SYNTH. Deionized water was used from Easy pure LF. The solvents acetone and ethanol (EtOH) were purchased from VETEC Química Fina LTDA and used without further purification.

A literature procedure was used for the preparation of xerogel silica.[4,5] The xerogel preparation in the presence of IL was performed under ambient conditions. TEOS (30 mL) was heated in a beaker to 60°C. A solution of IL (3.0 mL) in EtOH (15.0 mL) was added under stirring at 60°C, followed by aqueous HF (4.4×10^{-4} *M*, 7.5 mL). The beaker was covered with a watch glass and the reaction mixture was stirred for 10 min at 60°C. The reaction mixture was left at 60°C without stirring until dryness. The xerogel was obtained as a fine white powder and dried under vacuum for 5 h at 80°C (xerogel silica-ionic liquid hybrid **S1**). A soxhlet extraction with acetone for 24 h was performed. The extracted xerogel was dried under vacuum for 5 h at 80°C and calcined at 700°C for 2 h (silica **S2**).

The iPP and dried xerogel were melt blended using a preheated (180°C) twin rollers mill (Haake Rheomix 600) at 60 rpm. The rollers were activated, iPP (45 g) was added and molten during 5 min, and silica (3 wt %, not including the IL mass) was added. The mixture was mixed and heated for another 5 min at 180°C.

Thermal gravimetric analysis (TGA) was performed on a TA Instruments Q50 thermogravimetric analyzer. The TGA instrument was calibrated using nickel. An average sample weight of 8–12 mg was placed in a platinum pan and heated at 20°C/min from ~ 30 to 800°C under a flow of nitrogen or air.

The xerogels were analyzed by scanning electron microscopy (SEM) using a JEOL model JSM 5800 with 20 kV.

The polymer/composite phase transitions were determined using a TA Instruments DSC 2010 differential scanning calorimeter. The DSC instrument was calibrated using indium. An average sample weight of 5–10 mg was sealed in an aluminum pan. The samples were heated from 30 to 200°C at a heating and cooling rate of 10°C/min under a flow of nitrogen. The crystallization temperature (T_c, determined at the maximum of the exothermic peak) was determined in the first cooling run after removal of the thermal memory in the first heating run. The melting point (T_m, determined at the maximum of the endothermic peak) was determined in the second heating run.

Films for transmission electron microscopy (TEM) were obtained by compression molding of the polymer/composite to 190°C for 5 min at a pressure of 70 lbs. The samples were removed from the mold and cooled to room temperature. Ultra thin sections (50 nm thickness) of the specimens were obtained by cryoultramicrotomy with a diamond knife. TEM was carried out on a JEOL JEM-120 EXII TEM microscope operating at an accelerating voltage of 80 kV. The cuts were placed on 300 mesh Cu grids.

RESULTS AND DISCUSSION

Xerogel silica **S1** was prepared by the sol-gel technique, using TEOS as precursor and hydrofluoric acid as catalyst, in the presence of IL 1-decyl-3-methylimidazolium tetrafluoroborate. This sol-gel reaction yielded 4.0 g silica-IL hybrid after a gelation time of 12 h and ageing/drying time of 12 h. Its

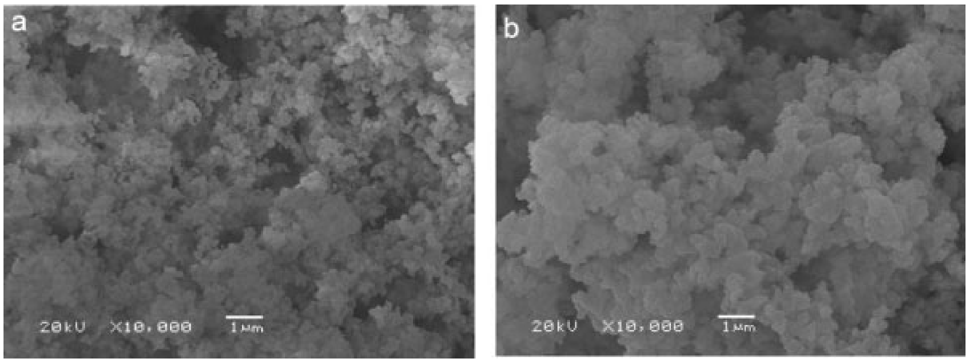

Figure 2 SEM micrographs of (a) **S1** and (b) **S2** at a magnification of ×10.000 (scale bar = 1 μm).

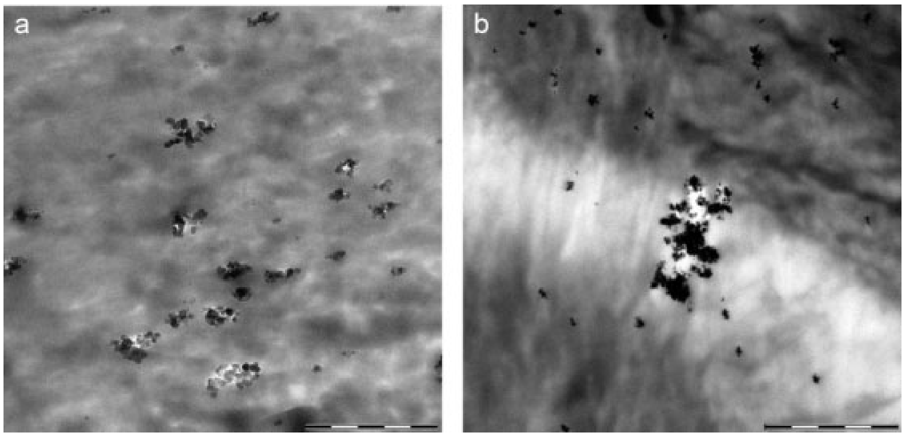

Figure 3 TEM micrographs of (a) **C1** and (b) **C2** at a magnification of ×13.500 (scale bar = 2 μm).

visual appearance was the same as previously obtained in the presence of IL 1-monoethylene glycol monomethyl ether-3-methylimidazolium tetrafluoroborate.[4] Silica **S1** was obtained as a free flowing white powder. A SEM study provided insight into the role of the IL as morphology controller [Fig. 2(a)]. 1-Decyl-3-methylimidazolium tetrafluoroborate induced the formation of a xerogel that consisted of aggregated spherical particles. Silica **S1** was subjected to an acetone extraction and calcination for a complete removal of the IL (silica **S2**). Comparison of the SEM micrographs (Fig. 2) shows that the silica **S1** surface was coated with an IL layer. TGA was performed to determine the IL content of hybrid **S1**, which was 30 wt %.

iPP was melt blended with the silica's **S1-2** to obtain the composites **C1** (**S1)** and **C2** (**S2**). This allowed studying the role of the IL in the formation of iPP composites. A TEM study was performed and Figure 3 shows representative TEM micrographs of the composites **C1-2**. The silica particles of composite **C2** were less dispersed in the polymer matrix in the absence of IL [Fig. 3(b)]. Besides, larger agglomerates were observed with a higher compactness (higher contrast of the silica particles in the TEM micrograph). In contrast, a higher degree of silica dispersion was achieved in composite **C1** [Fig. 3(a)]. Now, mainly smaller and less compact (lower contrast of the silica particles in the TEM micrograph) agglomerates were identified in the polymer matrix. This lower compactness of the silica particles indicates that IL 1-decyl-3-methylimidazolium tetrafluoroborate played an important role in the formation of composite **C1** and reduced the silica-iPP interfacial repulsion. Altogether, the observed effects of the IL could be due to a combination of factors. The combination of the tetrafluoroborate anion and imidazolium heterocycle hydrogen's are known to interact with silica surfaces via hydrogen bonding.[7] As a consequence; the decyl side-chain is most likely directed away from the silica surface. This apolar IL part is ready to interact with the apolar iPP and, as such, the IL could act as coupling agent, reducing the silica-iPP interfacial repulsion (Fig. 1). Furthermore, the IL coating on the silica surface could serve as protective layer for further silica aggregation. This is a benefit of the applied *in situ* technology for the hybrid preparation.

The thermal properties (Table I) of the composites **C1-2** and iPP were studied by DSC and TGA. Figure 4(a) represents the exothermic events of the crystallization temperature. The calcined silica of composite

TABLE I
Polymeric Composites of iPP and Silica

Entry	*S*[a]	% IL[b]	Composite	% SiO_2[c]	T_m (°C)[d]	T_c (°C)[e]	T_d (°C)[f]
1	**S1**	30	**C1**	3.5	167	120	388
2	**S2**	0	**C2**	2.7	158	113	362
3	–	–	–	–	167[g]	112[g]	334[g]

[a] Silica.
[b] IL content in wt % determined by TGA.
[c] Composite silica content determined by TGA.
[d] Melting point determined by DSC.
[e] Crystallization temperature determined by DSC.
[f] Decomposition temperature determined at loss of 5 wt % by TGA.
[g] Values for processed iPP.

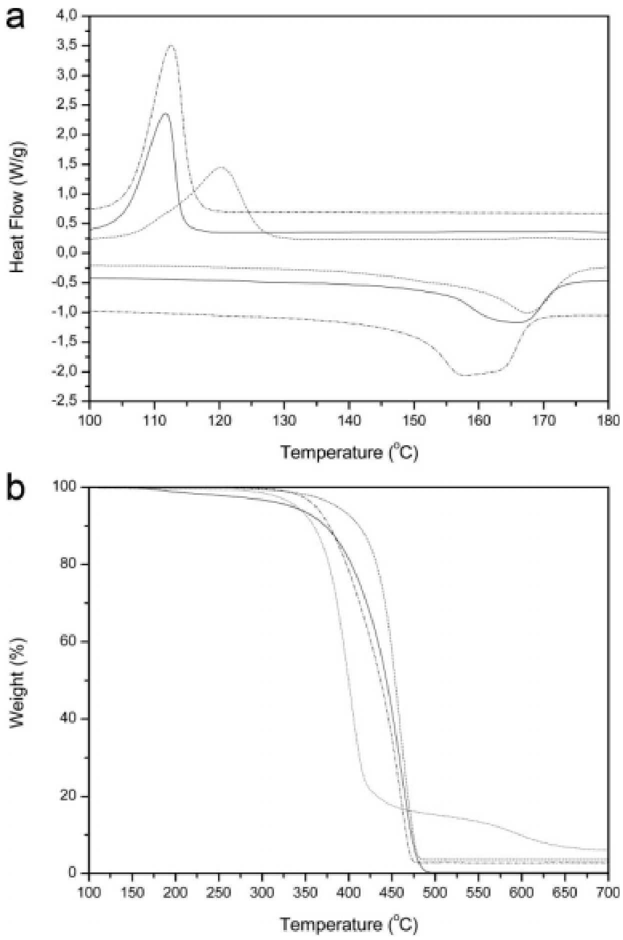

Figure 4 (a) DSC: Crystallization exotherms and melting endotherms of iPP (–), **C1** (- -) and **C2** (- ·); and (b) TGA: Thermal decomposition profiles of iPP (–), **C1** (- -) and **C2** (-·); and thermooxidative decomposition profile of **C1** (····).

C2 did not affect the crystallization temperature. Interestingly, the crystallization temperature of composite **C1** increased ~ 8°C. This fact could be related to the increased number of nucleation points within the polymer matrix, facilitating the formation of oriented polymer chains, which is another indication that the ionic liquid enhanced the interaction between the silica filler and polypropylene.[8] The endothermic events of the melting temperature are presented in Figure 4(a). No significant difference was observed between composite **C1** and iPP. However, composite **C2** showed a bimodal event, which could be due to the heterogeneous silica distribution in the polymer matrix. The resistance to thermal decomposition was dramatically affected by the silica incorporation [Fig. 4(b)]. Pure iPP started loosing weight at relatively low temperatures and lost 5 wt % at 334°C. The composites **C1-2** showed improved performances and the initial decomposition temperature profiles of the composites **C1-2** were similar until 340°C. After this temperature the resistance to thermal decomposition of composite **C1** was superior. Furthermore, the thermooxidative profile of composite **C1** was determined and is shown in Figure 4(b). Importantly, weight loss due to thermooxidation was insignificant at the processing temperature of 180°C. This shows that all components of composite **C1** are sufficiently stable for melt blending with iPP, including the applied ionic liquid.

CONCLUSIONS

1-Decyl-3-methylimidazolium tetrafluoroborate salt was identified as liquid coupling agent for the preparation of iPP-silica composites. Application of the IL coated silica hybrid **S1** in the melt blending procedure with polypropylene was responsible for a higher degree of dispersion in composite **C1** and a lower compactness of the silica particles. This composite was characterized by an increased crystallization temperature and an increased resistance towards thermal decomposition. As such, it is possible to obtain polymeric composites with differentiated properties with the presented technology. Altogether, this further expands the application scope of ILs in material science.

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References

1. Tjong, T. S. Mater Sci Eng 2006, R53, 73.
2. Thostenson, E.; Li, C.; Chou, T. J Compos Sci Tech 2005, 65, 491.
3. Zou, H.; Wu, S.; Shen, J. Chem Rev 2008, 108, 3893.
4. Donato, R. K.; Migliorini, M. V.; Benvegnú, M. A.; Stracke, M. P.; Gelesky, M. A.; Pavan, F. A.; Schrekker, C. M. L.; Benevenutti, E. V.; Dupont, J.; Schrekker, H. S. J Sol-Gel Sci Technol 2009, 49, 71.
5. Migliorini, M. V.; Donato, R. K.; Benvegnú, M. A.; Gonçalves, R. S.; Schrekker, H. S. J Sol-Gel Sci Technol 2008, 48, 272.
6. Schrekker, H. S.; Silva, D. O.; Gelesky, M. A.; Stracke, M. P.; Schrekker, C. M. L.; Gonçalves, R. S.; Dupont, J. J Braz Chem Soc 2008, 19, 426.
7. Zhou, Y.; Schattka, J. H.; Antonietti, M. Nano Lett 2004, 4, 477.
8. Huang, L.; Zhan, R.; Lu, Y. J Rein Plast Comp 2006, 25, 1001.