Improving the Metal Ion Release from Nanoparticles Embedded in a Polypropylene Matrix for Antimicrobial Applications

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ABSTRACT: Novel antimicrobial materials can be produced by adding copper nanoparticles (CNPs) into a polymeric matrix. To improve the behavior of these systems, the effect of different variables on the dispersion of copper metal nanoparticles embedded in a polypropylene matrix by melt mixing and its ion release was analyzed. The variables studied were predispersion of particles in liquid solvents, polymer molecular weight, melt mixing conditions, addition of a compatibilizer agent, two-step melt mixing, and surface functionalization of the metal particles. Our results show that by modifying these variables, a significant improvement in the filler dispersion, as quantified by optical microscope, can be obtained. For instance, the original CNP agglomerates can be reduced from an average size of 70 μm to a final average size of 30 μm and a larger amount of nanometric agglomerates by using a compatibilizer or predispersed nanoparticles. Moreover, by using surface-functionalized CNPs, micrometric agglomerates were not observed. Noteworthy, there is a direct relationship between the filler dispersion and the release of biocide copper ions when improvements were larger than a certain threshold with increases as high as 40%. These findings can be used in the development of antimicrobial materials with tailored behavior. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41232.

INTRODUCTION

A growing demand for novel materials able to reduce microbial infections should be expected as it represents today a nonresolved issue. In particular, healthcare-acquired infections (HAIs) still remain a major problem leading to prolonged hospital stay, increased morbidity and mortality for patients, and increased costs for the healthcare system.[1] It is estimated that between 5 and 10% of all hospitalizations are complicated by these nosocomial infections.[2] HAIs with the highest impact on the healthcare systems are septicemia, surgical site infection, catheter-associated urinary tract infections, ventilator-associated pneumonia, central line–associated bloodstream infection, and postoperative wound infection.[3] A study estimated around 1,700,000 nosocomial infections in the United States in 2002.[4,5] A more recent study reported that during 2009 around 440,000 cases were associated with the five major HAIs among US adult inpatients (including ICUs) at acute care hospitals.[3] *Staphylococcus aureus* is the most common cause of surgical site infection, and increasingly methicillin-resistant *Staphylococcus aureus* (MRSA) accounts for a greater proportion of infections in many hospitals throughout the world.[6]

A large percentage of HAIs are spread through surface contact (such as hands) or by catheters, intravenous lines, or surgical incisions. About 2–5% of all surgical patients develop a significant infection at the wound site, and 80–95% of hospital-acquired urinary tract infections originate from urinary catheters.[4,7] Contaminated environmental surfaces, such as bedside rails, are an under-recognized source of hospital infections.[4,8,9] In rooms of patients with diarrhea, viable MRSA and vancomycin-resistant Enterococcus have been collected from 59% and 46% of the room surfaces, respectively. Therefore, materials avoiding HAIs by surface contact, such as antimicrobial polymers, are necessary to be developed.

Antimicrobial polymers can be prepared by the incorporation of a biocide agent into bulk polymers during processing of the material or by applying surface coatings.[10–13] A different approach is the polymerization of monomer-containing biocide groups or the grafting of antimicrobial agents into the polymers.[10] Recently, the polymerization of the biocide polymer on the surface of commercial polymers by atom transfer radical polymerization has been reported.[14,15] From all the above-mentioned methods, the direct addition of the biocide agent into the polymers has received considerable attention especially for thermoplastics such as polyolefins.[16] This route can be easily implemented in the standard processing units already designed to prepare particulate filled polymer composites and that are

used extensively in the industry.[17] In this context, polymer/metal composites prepared by melt blending are perceived as a useful way to produce biocidal polymers as metals can be high toxic against a broad range of microorganisms.[18] Moreover, metals do not suffer degradation under the standard processing conditions of thermoplastic polymers (200°C).[16,19] From the different metals that can be used as filler in polymer matrices, copper emerges as an excellent candidate because of its good biocide properties, as showed recently using nanoparticles (copper nanoparticles [CNPs]).[20–23] Our group has shown that polypropylene/CNP composites prepared by melt blending present tailored antimicrobial behavior depending on the kind of CNP and its concentration.[24,25] Based on these results, a direct relationship between copper release rate and antimicrobial behavior was concluded as summarized in Figure 1, in which the inverse of the needed time to eliminate 50% of *Escherichia coli* bacteria is plotted against the release rate of copper ions. Samples releasing larger amount of ions display better antimicrobial behavior. In this context, the filler size in polymer/metal nanocomposites is relevant as shown by Damm and Munstedt concluding that nanoparticles embedded in a polymer matrix presented higher ion release rates than microparticles because of their extremely high specific surface area.[27] Xia et al.[28] observed the same behavior for pure copper particles where the larger specific surface area and the higher surface energy of nanoparticles, when compared with microparticles, were stated as the main reason for the differences observed. The interaction between copper and water is facilitated in nanoparticles because of its high surface energy as reported by these authors. Moreover, a CuO film was observed in microparticles retarding the corrosion processes, whereas in nanoparticles, a Cu_2O layer was formed that can be easily dissolved, explaining the behavior found.[24,28] These results stress the relevance of using metal CNPs in polymer composites for antimicrobial applications. The goal of this study is to improve the CNP dispersion in a polypropylene matrix and to relate this improvement with changes in the release of copper ions from the composite. The success of our goal will allow a future optimization of the antimicrobial behavior of polymer/metal composite materials.

MATERIALS AND METHODS

Preparation of Polypropylene/CNP Composites

The main polymeric matrix was a commercial grade isotactic polypropylene from PETROQUIM (Chile) with a melt flow rate (230°C/2.16 kg; Norm ASTM D-1238/95) of 3.3 g/10 min (PP03) having a weight–average molecular weight of 281.307 (g mol^{-1}) and polydispersity of 5.7. For the analysis of polymer molecular weight, polypropylene (PP) with melt indexes of 01 (PP01) and 13 (PP13) g/10 min was also used having weight–average molecular weights of 359.607 (g mol^{-1}) and 189.103 (g mol^{-1}) and polydispersities of 5.1 and 13.8, respectively. CNPs with an average particle size of 10 nm were supplied by Versus (Chile). The composites were prepared by using a Brabender plasticorder at 190°C, 110 rpm, and 10 min under nitrogen atmosphere to avoid oxidative degradation processes. The amount of CNP in the composites was 5 wt %. The composites were press molded at 190°C at 50 bar for 5 min and cooled under pressure by flushing the press with cold water. For the
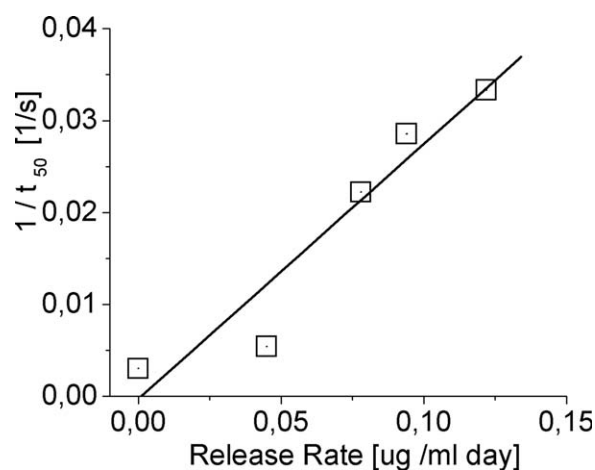

Figure 1. The inverse of the needed time to eliminate 50% of *E. coli* bacteria plotted against the release rate of copper ions based on Ref. 26.

ion release analysis, the samples were shaped into squares with dimensions of 50 mm × 50 mm and a final thickness around 1 mm. A commercial polypropylene grafted with 0.6 mol % content of maleic anhydride from Aldrich (PP-*g*-MA) was used as compatibilizer. In this case, a master batch containing a mixture of CNP and the compatibilizer with a weight ratio of 1:2 was prepared by using the Brabender plasticorder equipment under the same conditions as those used for the preparation of the pure composites. This method produced composites with particles embedded in the polymer matrix without any specific distribution.[25] Moreover, particles from the bulk of the composite release the copper ions as surface particles were not observed.[25]

Composite Characterization

The release of Cu^{2+} from the nanocomposites was quantified using a UV–Visible Agilent spectrophotometer (Model 8453; Agilent Technologies, Waldbroon, Germany) spectrophotometer. Samples were put in a solution of 100 mL of distilled water, and from this solution 10 mL was taken for analysis at different times. The ion concentration was determined by adding 1 mL of 10% hydroxylamine hydrochloride solution, 1 mL of sodium acetate–acetic acid buffer (pH = 4.5), and 1 mL of 1.92×10^{-3} mol neocuproine (copper reagent). The neocuproine was used to form a yellow chelate with the cupric ions, and a calibration of absorbance versus cupric ion was obtained by measuring the chelate solution of various $CuSO_4$ concentrations. Finally, the morphology of some nanocomposites was analyzed by a transmission electron microscopy (TEM) Philips model CM 100 at 80 kV. Ultrathin sections of about 70 nm were obtained by cutting the samples with an Ultracut Reichert-Jung microtome equipped with a Diatome diamond knife.

Because of both the large number of samples to characterize and the large size of the agglomerates formed, a Leica DML optical microscope was used to quantify the filler dispersion. This methodology focused on the size of the agglomerates and its number. For this analysis, films of around 100 μm thickness
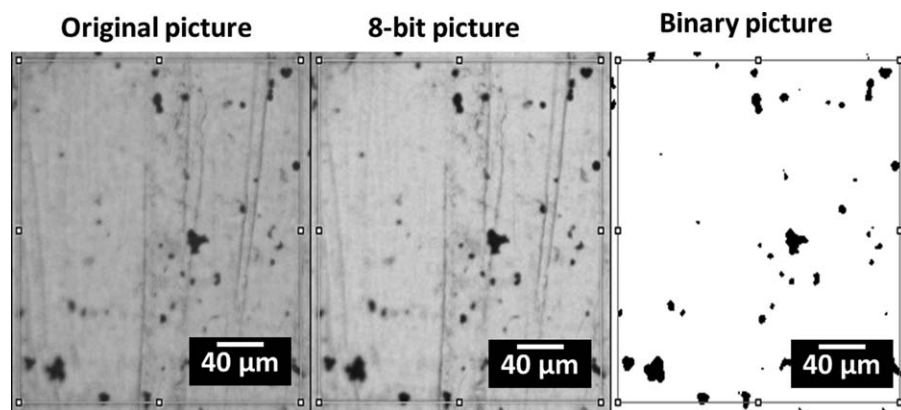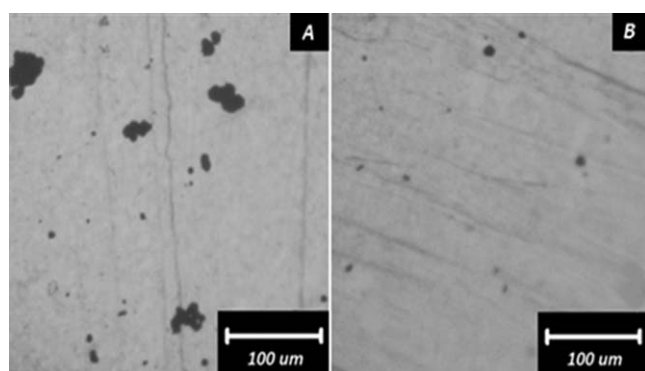
Figure 2. Example of the methodology used to quantify the filler dispersion by using optical microscope and Image J software package. The original photographs are transformed to binary pictures, going through a 8-bit transformation, where the value of black pixels (representing the particles) can be related with the size and number of agglomerations.

were observed in the optical microscope, and for each sample at least 15 pictures were taken. The Image J software package was used for the quantitative analysis of the photographs by transforming the original picture to binary pictures through an 8-bit transformation. The value of black pixels (representing the particles) was related with the size and number of agglomerates. Example of this methodology is shown in Figure 2.
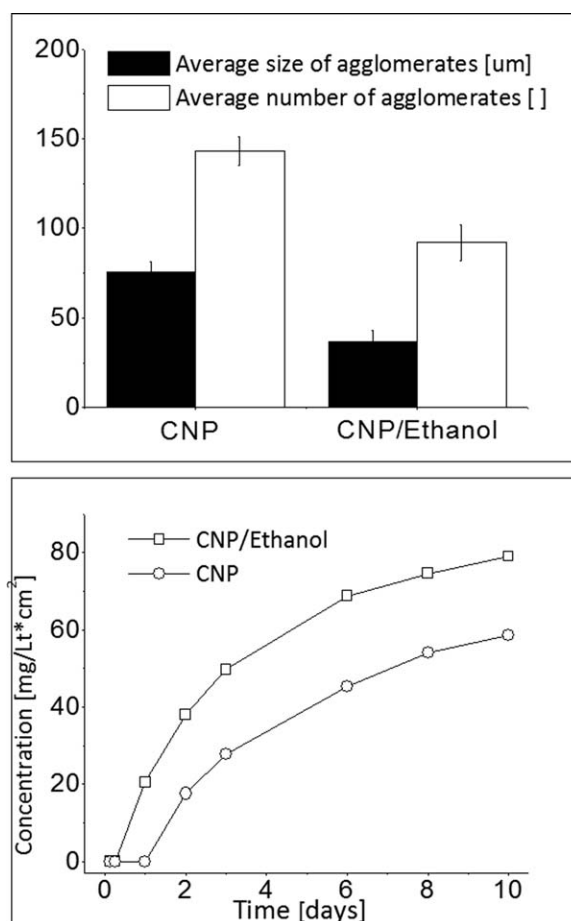
Surface Functionalization of CNP

To avoid the agglomeration of the CNP in the nonpolar matrix, CNPs were synthesized and stabilized by surface modifications following the procedure explained by Neckers and coworkers.[29] About 9.6 g of copper(II) chloride (97%; Sigma Aldrich) was dissolved in 200 mL of methanol (99.8%; Equilab). Afterward, 10.2 mL of hexanethiol (98%; Sigma Aldrich) was added dropwise into the solution, and the mixture was strongly stirred for 30 min under nitrogen. Subsequently, 35 mL of a 0.5 M solution of sodium ($NaBH_4$, 98%; Sigma Aldrich) was added dropwise into the reaction media with constant stirring. The mixture was stirred for 4 h at room temperature under nitrogen. Afterward, the solvent was removed, and the result was dispersed in ethanol and washed three times by centrifugation at 8000 rpm for 15 min. Finally, the particles were dried at 70°C. The aver-

age size of these particles is around 10 nm. Under this procedure, the functionalized CNPs have attached on its surface n-hexanethiol molecules by Cu—S bonds.[29] UV–vis absorption

Figure 4. Effect on the average size and number of agglomerates (top) and on the copper ion release (bottom) of composites prepared with CNP predispersed in ethanol when compared with the addition of filler as powder.

Figure 3. Optical micrographs showing the effect on the agglomerates of composites prepared with CNP predispersed in ethanol (B) when compared with the addition of filler as powder (A).
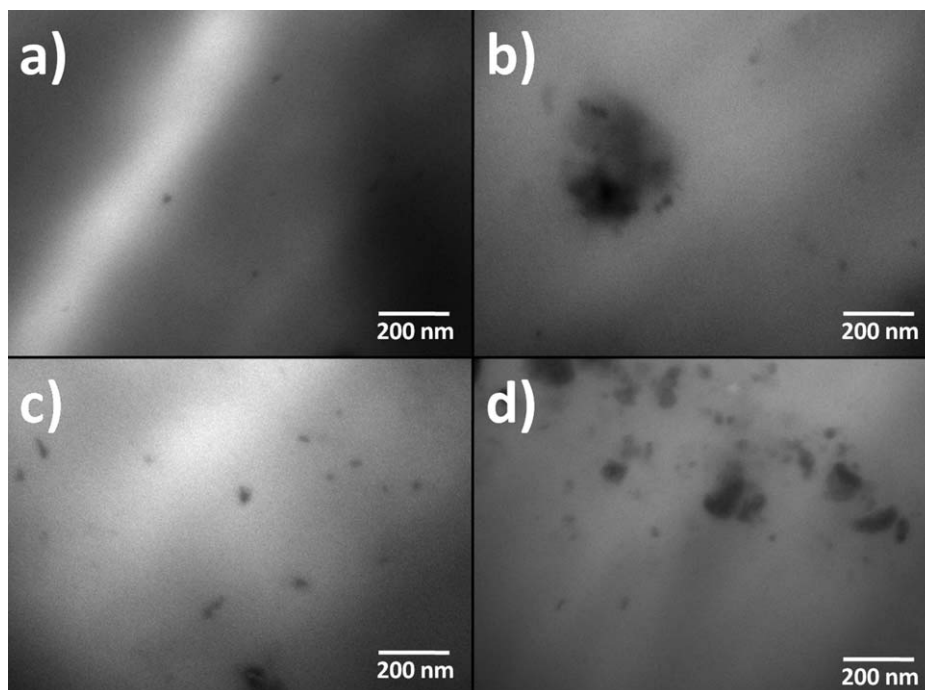
Figure 5. TEM images showing the morphology of composites prepared with CNP pretreated by dissolution in ethanol (C and D) when compared with the addition of filler as powder (A and B).

spectrum and X-ray diffraction patterns from these hybrid nanoparticles confirm this structure (results now shown).

RESULTS

### Effect of CNP Predispersed in Ethanol Solvent

The first variable studied is the predispersion of CNP before its addition into the polypropylene melt. In this case, the particles were dispersed in a solvent by ultrasonication at a concentration of 1 g L^{-1}. The behavior of CNP in different solvents such as methanol, xylene, water, and ethanol was studied. The stability of CNP in the different solvents after sonication for 60 s was evaluated by simple optical observation quantifying the time needed for the agglomerates of CNP to precipitate. The times were 30, 52, 54, and 80 s for methanol, xylene, water, and ethanol, respectively. Ethanol was therefore selected for this methodology having further the high volatility. The solution with the dispersed particles was directly added to the mixer with the polypropylene melt at 190°C. The temperature of the system was higher than the boiling temperature of the solvent, and ethanol was evaporated during the composite preparation. Figure 3 shows an example of the images obtained with the predispersion method where data from the direct addition to the melt mixer of CNP as powder are further displayed. From Figure 3 it is clear that CNP added as a powder leaded to large agglomerates with sizes from 20 to 70 μm together with small ones with sizes around 2 μm. By using the predispersion method, these large agglomerates were not observed as displayed in Figure 3 and only small agglomerates were present. This tendency was quantified by analyzing several pictures and taking the averages of the number of agglomerates evaluated at an area of 300 × 300 μm^2 and its sizes, as shown in Figure 4 (top). From this

analysis, it is concluded that the predispersion method allowed a drastic reduction in the average size of the agglomerates from 70 to 30 μm. Together with this size reduction, a larger number of small agglomerates could be expected. However, Figure 4 shows the opposite tendency as the number of agglomerates decreased from 140 to 90 units. This behavior can be explained assuming that the predispersion method generated agglomerates in the polymer with sizes smaller than the resolution of the optical microscope and therefore were not observed. To confirm this, TEM was used to analyze these samples as displayed in Figure 5. TEM images from composites prepared with CNP as powder showed both a low amount of individual particles and agglomerates with sizes around 200 nm. This low density of particles means that most of the particles formed large agglomerates as observed by optical microscope. However, by the predispersion method, a higher density of particles and nanometric agglomerates were observed by TEM, both having sizes smaller than the resolution of the optical microscope. On the basis of this analysis, we conclude that a reduction of the number of agglomerates, as observed by optical microscope (Figure 4), is an indicator of both a reduction of agglomerate sizes and an increased presence of individual CNP. Therefore, by using predispersed CNP particles, the dispersion of the filler is improved. Noteworthy, Figure 4 (bottom) shows that the improvement in the filler dispersion had as a consequence a larger ion release from the composite. The effect of the filler dispersion in this case is more relevant at short period of times (less than 3 days).

Effect of Matrix Molecular Weight

Figure 6 shows the effect of the matrix molecular weight comparing the behavior of the PP03-based composite with the composites prepared with polymers having either higher (PP01) or
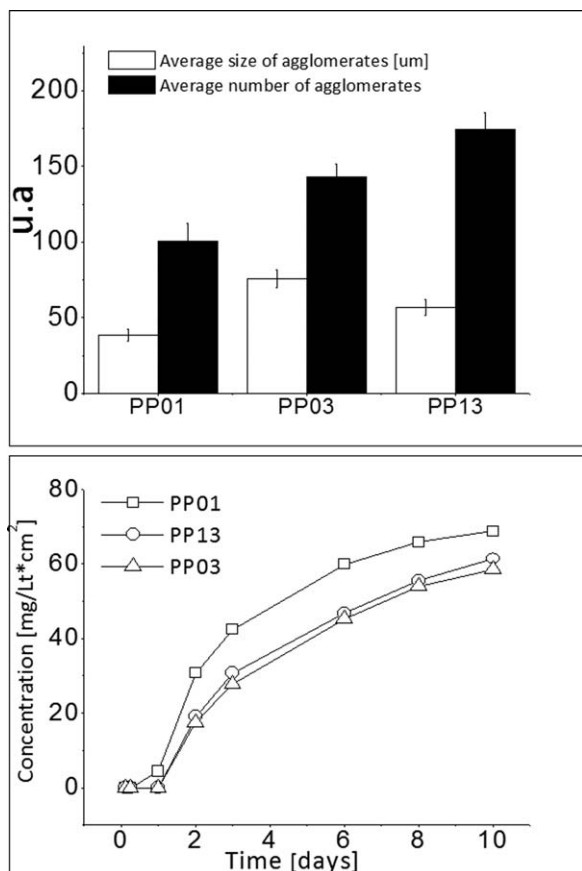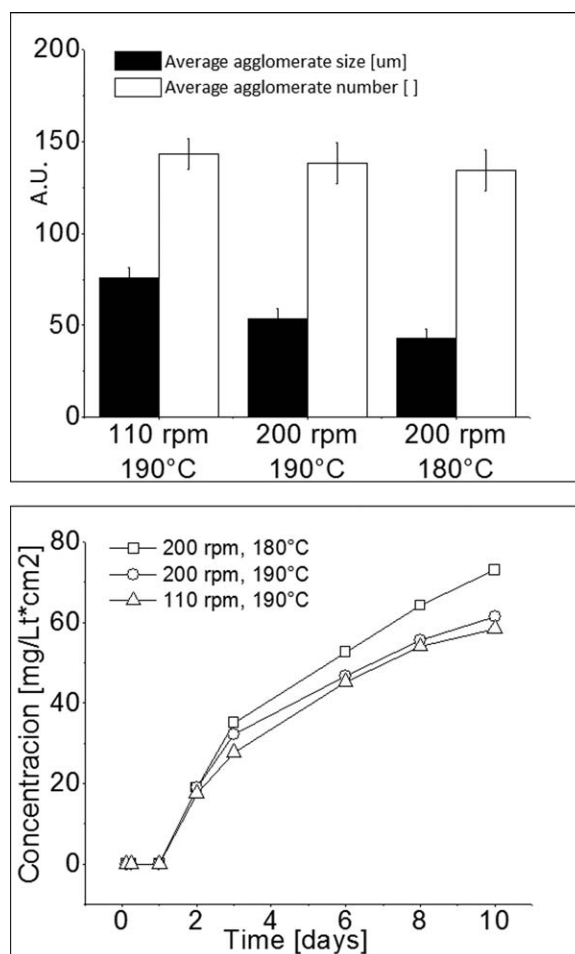
Figure 6. Effect on the average size and number of agglomerates (top) and on the copper ion release (bottom) of composites prepared with matrices of low (PP13), medium (PP03), and high (PP01) molecular weights.

molecular-weight chains as previously reported.[26] As the agglomerated were still in the micrometric range, the release of copper ions from PP13 composites was not affected for the improvement in the filler dispersion (Figure 6). These results indicated that improvements above some threshold were needed to obtain changes in the ion releases from the composites.

Effect of Melt Blending Conditions

The effect of the melt blending conditions was further studied increasing the mixing speed from 110 to 200 rpm, indicating larger shear stresses in the system.[26] At this high rpm, the agglomerates decreased its size from 75 to 50 μm although the number of agglomerates was unchanged (Figure 7, top). Similar to the results from composites based on PP13, the improvement in the filler dispersion was not enough to increase the copper ion release as observed in Figure 7. The mixing temperature was also analyzed decreasing its value from 190 to 180°C at 200 rpm. Under these conditions, the size of the agglomerates further decreased to 40 μm as a consequence of the increased viscosity. However, although the number of agglomerates did not change, these composites were able to slightly increase the copper ion release as observed in the bottom part of Figure 7.

lower (PP13) molecular weights. From the optical microscope analysis, it was concluded that composites prepared with PP01 displayed the lowest average size (∼ 40 μm) and number (∼ 100 units) of agglomerates. Therefore, an improvement in the filler dispersion was obtained by using high-molecular-weight polymers having as a consequence a higher release of copper ions (Figure 6, bottom). This improvement can be associated with the relationship between polymer molecular weight and its viscosity. In this way, agglomerates of CNP were exposed to higher shear stresses reducing its size.[26,30,31] Composites based on a low-molecular-weight matrix (PP13) presented a larger amount of agglomerates with lower sizes than the sample based on PP03 also indicating an improved filler dispersion. However, in this case, the new agglomerates were still in the micrometric range as observed by optical microscope. Therefore, low-molecular-weight polymers were able to interact with the agglomerates reducing its sizes although less than high-molecular-weight polymers. The agglomerates can be infiltrated by low-molecular-weight polymers affecting either the packing structure or the cohesive forces binding small agglomerates.[26,32] This infiltration phenomenon has also been reported in polypropylene composites based on carbon nanotubes.[33] The results displayed in Figure 6 showed that the final morphology of the filler was a balance between the infiltration of low-molecular-weight chains and the high shear stress transferred by high-
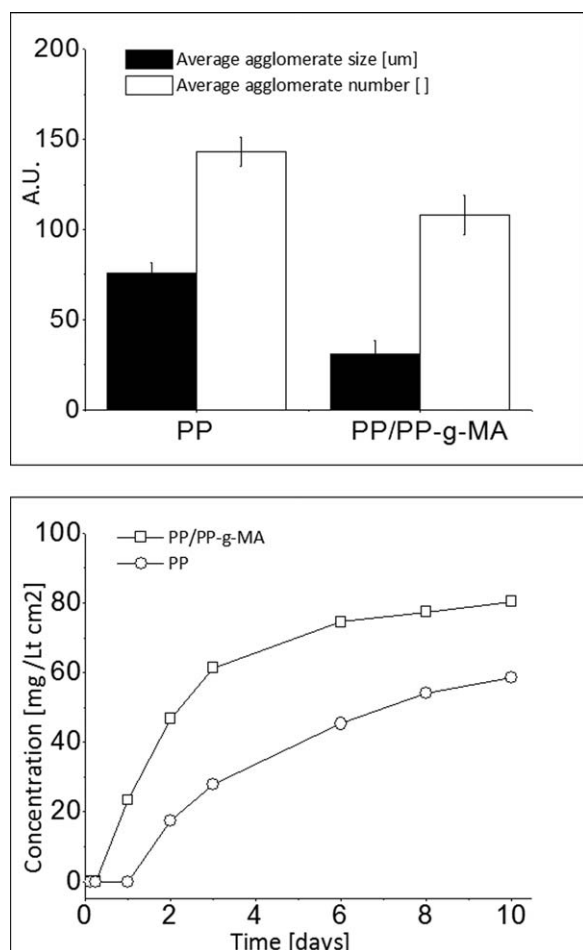

Figure 7. Effect on the average size and number of agglomerates (top) and on the copper ion release (bottom) of composites prepared under different melt mixing conditions.

Figure 8. Effect on the average size and number of agglomerates (top) and on the copper ion release (bottom) of the presence of a compatibilizer.

Effect of Compatibilizer

A well-known methodology to improve the filler dispersion is the addition of a compatibilizer, in this case a polypropylene grafted with maleic anhydride (PP-g-MA). First, a master batch containing PP-g-MA with 33 wt % of CNP was prepared by melt mixing and diluted afterward with pure PP03 in another melt mixing process. Figure 8 shows that the addition of a compatibilizer drastically improved the filler dispersion reducing the size and number of the agglomerates from 75 to 35 μm and from 140 to 110 units, respectively. Similar to our previous results, this improvement in the filler dispersion rendered a relevant increase in the release of copper ions as displayed in the bottom part of Figure 8. However, the double mixing process (the first during the preparation of the master batch and the second during the dilution process), rather than the presence of a compatibilizer, could explain the filler dispersion. To analyze the real contribution of the double mixing process, a master batch with PP03, instead of PP-g-MA, was prepared and afterward diluted with PP03. In this case, the size of the agglomerations was reduced from 75 to 45 μm, whereas the number of agglomerates increased from 140 to 160 units, indicating an improvement in the dispersion although less than using the

compatibilizer. The same occurred with the copper ion release, where a slight improvement was observed although not as high as the obtained by using the compatibilizer. Therefore, the synergic effect of the double mixing and the compatibilizer was responsible for the high improvement observed in Figure 8.

The method used to prepare the master batch, with either PP-g-MA or PP03, was further studied by comparing the melt mixing method with the dissolution mixing method using xylene as solvent at 120°C. In this case, the polymer was dissolved in xylene at 120°C, and afterward, the particles were added predispersed in xylene (5 g L^{-1}). The polymer/particle system was precipitated with ethanol and dried generating the master batch. The composites were prepared by melt mixing method. The results are displayed in Figure 9 and compared with the direct addition of CNP as powder. Both master batches were able to improve the dispersion reducing the agglomerate sizes from 75 to 45 μm, whereas the number of agglomerates did not change. These improvements had as a consequence similar increment in the release rates of copper ions. Therefore, by dissolution method, the effect of the compatibilizer is neglected as the same results were obtained using the pure matrix. Moreover, the results from master batches prepared by dilution mixing were as similar as those prepared by melt mixing.

Effect of Surface Functionalization of CNP

The last variable studied was the surface functionalization of CNP following the synthesis described by Neckers and coworkers.[29] In this case, a perfect dispersion was obtained as
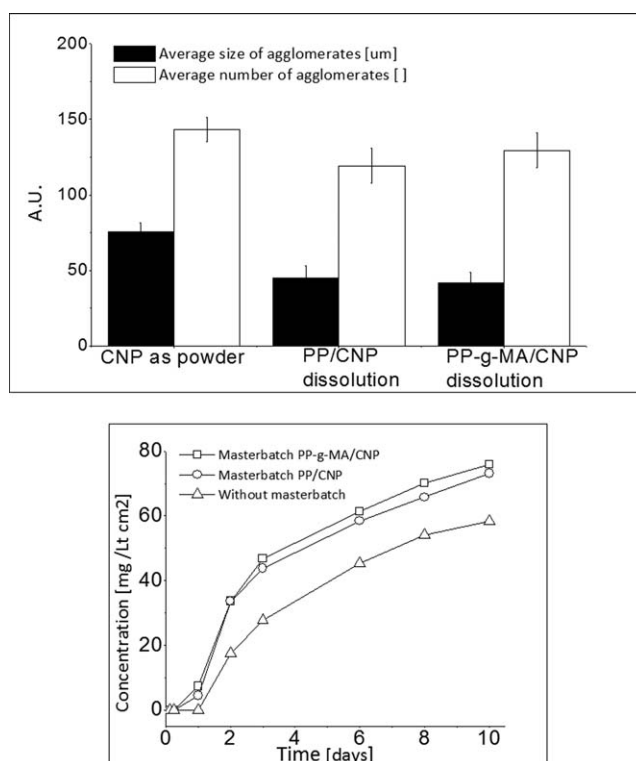
Figure 9. Effect on the average size and number of agglomerates (top) and on the copper ion release (bottom) of using master batches prepared by dissolution mixing using Xilene at 120°C. Two master batches were studied, one prepared with PP-g-MA and another prepared with PP03.

agglomerates or particles were not observed by optical microscope as displayed in Figure 10. This improvement in the filler dispersion explains the increase in the release rate of the composites with 5 wt % of functionalized nanoparticles (Figure 10, bottom). Noteworthy, the ion release from these composites with modified nanoparticles is higher considering the filler composition: 50 wt % of copper and 50 wt % of organic modifiers.

General Mechanism for the Antimicrobial Effect of Polypropylene/CNT Composites

These results allowed the conclusion that the dispersion of CNP in a polypropylene matrix depends on several factors as summarized in Table I. Moreover, Table I shows that the improvement in the dispersion state of CNP dramatically increases the release of copper ions from the nanoparticles embedded in the polymer matrix. This effect has practical consequences on the antimicrobial behavior of these nanocomposites as metal ions are considered the effective active agent killing the bacteria. Several studies show the antimicrobial behavior of metal nanoparticles against microorganisms, although the exact mechanism is not clearly known.[29,34–37] In general, for metal-based nanoparticles, the proposed mechanisms of toxicity can be separated into two depending of the species considered as the active agent: (1) the metal nanoparticle or (2) the metal ions released
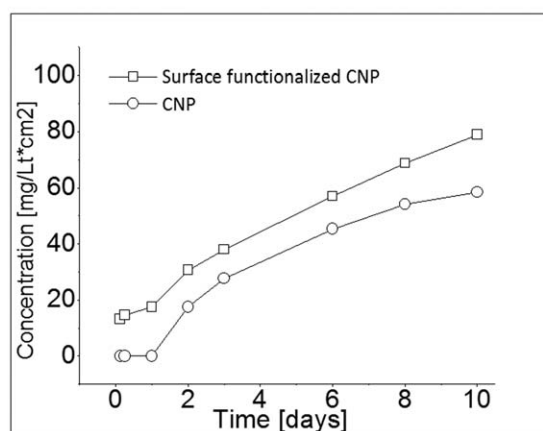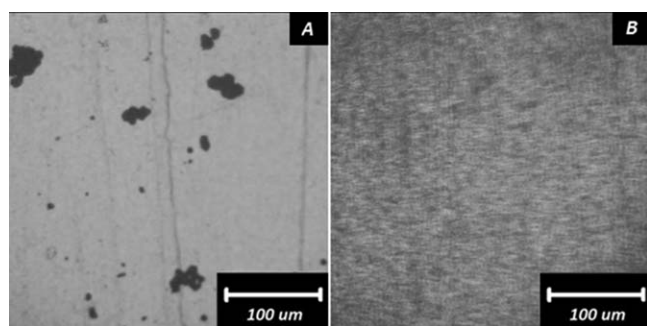
Table I. Summary of the Effect of the Main Variables Studied on the Dispersion of Copper Nanoparticle and the Ion Release of Polypropylene Composites

Method	Average size of agglomerates (μm)	Copper release after 10 days (μg L^{-1} cm^{-2})
Using CNP powder (standard)[a]	75	56
CNP predispersed in ethanol	30	80
Using a matrix of high molecular weight	40	70
Using a matrix of low molecular weight	50	55
Improving the melt mixing conditions[b]	40	75
Using a compatibilizer	30	78
Using functionalized CNP	Not detected	80

[a] Matrix PP03, melt mixer operating at 110 rpm and 190°C.
[b] Matrix PP03, melt mixer operating at 200 rpm and 180°C.

from the particles.[37] The first mechanism is based on the "Trojan-horse" effect where, for instance, CNPs can penetrate to the cell wall releasing inside its ions.[37,38] However, a growing number of reports indicate that the ion release is the driving force behind the antimicrobial properties of antibacterial nanoparticles.[18,39] This approach is supported by recent results from copper oxide nanoparticles showing the absence of the Trojan-horse effect.[37] In fact, most of the analyses regarding antimicrobial metal nanoparticles focused on the metal ion release instead of the particle absorbed by the bacteria.[29,34,35] This was confirmed by the results coming from polymer/metal nanocomposites where the antimicrobial effect of these materials related with the metal ion releases rather than with the leaching of the particle.[24,25] The same tendency was observed in Figure 1.

CONCLUSIONS

A systematic study about the effect of different parameters on the dispersion of metal nanoparticles embedded in a polymer matrix was conducted relating the filler agglomeration with the release of ions from the composite. Our results showed that improvements in the dispersion of CNPs in a polypropylene matrix can be obtained by predispersing the particles, changing the matrix molecular weight, using a compatibilizer, double melt mixing, dissolution method, and surface functionalization of the particles. In particular, the original CNP agglomerates having an average size of 70 μm were drastically reduced by either predispersing the particles in ethanol or using a compatibilizer with a final average size of 30 μm and a larger amount of nanometric agglomerates. Moreover, by using surface-functionalized CNP, micrometric agglomerates were not observed. Noteworthy, the improvement in the filler dispersion produced increases as high as 40% in the copper ion release from the composites allowing the optimization of the antimicrobial behavior of these composites.

Figure 10. Effect on filler dispersion as evaluated by optical microscope (top) and on copper ion release (bottom) of the surface functionalization of CNP. The plot shows the release from composites with 5 wt % of filler, which means that in composites based on functionalized particles, the effective copper concentration is 2.5% w/w.

REFERENCES

1. Leth, R. A.; Møller, J. K. *J. Hosp. Infect.* **2006**, *62*, 71.

2. Balkhya, H. H.; Cunninghama, G.; Chewa, F. K.; Francis, C.; Nakhli, D. J. A.; Almuneef, A. M. A.; Memish, Z. A. *Int. J. Infect. Dis.* **2006**, *10*, 326.

3. Zimlichman, E.; Henderson, D.; Tamir, O.; Franz, C.; Song, P.; Yamin, C. K.; Keohane, C.; Denham, C. R.; Bates, D. W. *JAMA Int. Med.* **2013**, *173*, 2039.

4. Curtis, L. T. *J. Hosp. Infect.* **2008**, *69*, 204.

5. Klevens, R. M.; Edwards, J. R.; Richards, C. L.; Horan, T. C.; Gaynes, R. P.; Pollock, D. A.; Cardo, D. M. *Public Health Rep.* **2007**, *122*, 160.

6. Humphreys, H. *J. Hosp. Infect.* **2009**, *73*, 316.

7. Cheadle, W. G. *Surg. Infect.* **2006**, *7*, S7.

8. Boyce, J. M. *J. Hosp. Infect.* **2007**, *65*, 50.

9. Beard-Pegler, M. A.; Stubbs, E.; Vickery, A. M. *J. Med. Microbiol.* **1988**, *26*, 251.

10. Kenawy, E. R.; Worley, S. D.; Broughton, R. *Biomacromolecules* **2007**, *8*, 1359.

11. Zhang, W.; Zhang, Y. H.; Ji, J. H.; Zhao, J.; Yan, Q.; Chu, P. K. *Polymer* **2006**, *47*, 7441.

12. Jones, D. S.; Djokic, J.; Gorman, S. P. *Biomaterials* **2005**, *26*, 2013.

13. Yuan, Y. L.; Ai, F.; Zang, X. P. *Colloid Surf. B* **2004**, *35*, 1.

14. Huang, J.; Murata, H.; Koepsel, R. R.; Russell, A. J.; Matyjaszewski, K. *Biomacromolecules* **2007**, *8*, 1396.

15. Lee, S. B.; Koepsel, R. R.; Morley, S. W.; Matyjaszewski, K.; Sun, Y.; Russel, A. J. *Biomacromolecules* **2004**, *5*, 877.

16. Appendini, P.; Hotchkiss, J. H. *Inn. Food Sci. Emerg. Technol.* **2002**, *3*, 113.

17. Pehlivan, H.; Balkose, D.; Ulku, S.; Tihminlioglu, F. *Compos. Sci. Technol.* **2005**, *65*, 2049.

18. Lemire, J. A.; Harrison, J. J.; Turner, R. J. *Nat. Rev. Microb.* **2013**, *11*, 371.

19. de Azeredo, H. M. C. *Food Res. Int.* **2009**, *42*, 1240.

20. Wilks, S. A.; Michels, H.; Keevil, C. W. *Int. J. Food Microb.* **2005**, *105*, 445.

21. Faundez, G.; Troncoso, M.; Navarrete, P.; Figueroa, G. *BMC Microb.* **2004**, *4*, 19.

22. Mulligan, A. M.; Wilson, M.; Knowles, J. C. *Biomaterials* **2003**, *24*, 1797.

23. Borkow, G.; Gavia, J. *Curr. Med. Chem.* **2005**, *12*, 2163.

24. Delgado, K.; Quijada, R.; Palma, R.; Palza, H. *Lett. Appl. Microbiol.* **2011**, *53*, 50.

25. Palza, H.; Gutiérrez, S.; Delgado, K.; Salazar, O.; Fuenzalida, V.; Avila, J.; Figueroa, G.; Quijada, R. *Macromol. Rapid Commun.* **2010**, *31*, 563.

26. Kasaliwal, G. R.; Göldel, A.; Pötschke, H. G. *Polymer* **2011**, *52*, 1027.

27. Damm, C.; Munstedt, H. *Mater. Chem. Phys.* **2008**, *108*, 61.

28. Xia, X.; Xie, C.; Cai, S.; Yang, Z.; Yang, X. *Corros. Sci.* **2006**, *48*, 3924.

29. Anyaogu, K. C.; Fedorov, A. V.; Neckers, D. C. *Langmuir* **2008**, *24*, 4340.

30. Fornes, T. D.; Yoon, P. J.; Keskkula, H.; Paul, D. R. *Polymer* **2001**, *42*, 9929.

31. Gianelli, W.; Ferrara, G.; Camino, G.; Pellegatti, G.; Rosenthal, J.; Trombini, R. C. *Polymer* **2005**, *46*, 7037.

32. Yamada, H.; Manas-Zloczower, I.; Feke, D. L. *Powder Technol.* **1997**, *92*, 163.

33. Micusík, M.; Omastová, M.; Krupa, I.; Prokes, J.; Pissis, P.; Logakis, E.; Pandis, C.; Potschke, P.; Pionteck, J. *J. Appl. Polym. Sci.* **2009**, *113*, 2536.

34. Ren, G.; Hub, D.; Cheng, E. W. C.; Vargas-Reus, M. A.; Reipd, P.; Allaker, R. P. *Int. J. Antimicrob. Agents* **2009**, *33*, 587.

35. Ruparelia, J. P.; Chatterjee, A. K.; Duttagupta, S. P.; Mukherji, S. *Acta Biomater.* **2008**, *4*, 707.

36. Yoon, K. Y.; Byeon, J. H.; Park, J. H.; Hwang, *J. Sci. Total Env.* **2007**, *373*, 572.

37. Prabhu, S.; Poulose, E. K. *Int. Nano Letters* **2012**, *2*, 32.

38. Karlsson, H. L.; Cronholm, P.; Gustafsson, J.; Moller, L. *Chem. Res. Toxicol.* **2008**, *21*, 1726.

39. Gunawan, C.; Teoh, W. Y.; Marquis, C. P.; Amal, R. *ACS Nano* **2011**, *5*, 7214.