

The Influence of the Different Modifying Agents on the Synthesis of Poly(methylmethacrylate)-Calcium Carbonate Nanocomposites via Soapless Emulsion Polymerization

Xiaokun Ma, Yanhua Liu, Yang Yu, Hong Lei, Xiaotang Lv, Lina Zhao, Suxia Ren, Zichen Wang

Institute of Chemistry, Jilin University, Changchun 130023, People's Republic of China

Received 20 June 2007; accepted 5 November 2007

DOI 10.1002/app.27812

Published online 23 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of poly(methylmethacrylate)-calcium carbonate nanocomposites via the soapless emulsion polymerization was investigated after the CaCO_3 nanoparticles were modified with different modifying agents. Such three kinds of modifying agents as sodium stearate (SS), oleic acid (OA), and PMMA were used to improve the surface property of CaCO_3 nanoparticles. What was the most important factor to improve the amount of nanoparticles in the composites is one of the general goals. As determined by Field-emission scanning electron microscopy (FESEM), the nanocomposites size of the diluted polymer emulsion was over 250 nm, while the sample without CaCO_3 had a diameter of about 150 nm. It was worth pointing out that the surface morphology of polymer changed from slick to scraggy, when the nano- CaCO_3 particles participated in the polymerization process. The increase of the

droplet size and the change of the polymer morphology indicated that the CaCO_3 nanoparticles were present in the emulsion droplets. The X-ray diffraction results of the nanocomposites showed the existence of typical calcite peaks. The results of the TGA, FTIR, and the contact angles indicated that the hydrophobic surface of CaCO_3 nanoparticles was crucial to improve the compatibility between the CaCO_3 and MMA monomer in emulsion system. The results of the TGA, FTIR, and the contact angles indicated that the hydrophobic surface of CaCO_3 nanoparticles was crucial to improve the compatibility between the CaCO_3 and MMA monomer in emulsion system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1421–1425, 2008

Key words: compatibility; composites; filler; emulsion polymerization; surfactants

INTRODUCTION

The incorporation of inorganic particles into polymers allows one to integrate new functions inside polymer matrices. Polymer composites are widely applied in the areas such as transportation, construction, electronics, and consumer products.^{1–8} However, the properties of particle-reinforced polymer composites are strongly influenced by the dimensions and microstructure of the nanofillers. In recent years, with the development of the nanotechnology, more and more nanofillers have been loaded in the polymer matrices to synthesize the innovative advanced materials.

Calcium carbonate makes an attractive mineral for studies in the laboratory, since its crystals are easily characterized and the morphology of CaCO_3 could be controlled in carbonation processes. Calcium carbonate is one of the cheapest commercially available inorganic filler, which makes it a great interest for industrial and technological applications.^{9–12}

The synthesis of poly(methyl methacrylate) (PMMA)- CaCO_3 nanocomposites has been reported very recently using a variety of surfactants, dispersion techniques, and polymerization conditions.^{13–17} The soapless emulsion polymerization has the advantage that all the ingredients are added to a single reactor and the fewer surfactants are able to avoid the disadvantage in the polymer processing. At the same time, one step that is necessary when using an *in situ* polymerization technique: CaCO_3 treatment.

In this article, the CaCO_3 nanoparticles were modified with sodium stearate (SS), oleic acid (OA), and PMMA. SS and OA could interact with CaCO_3 nanoparticles, which changed the surface property of the nano- CaCO_3 particles from hydrophilic to hydrophobic. At the same time, an unsaturated C=C chemical bond could be introduced to the CaCO_3 nanoparticles after the modification with OA. While the PMMA as a modifying agent only improved the compatibility between the CaCO_3 particles and polymer matrix. We have reported that the possible mechanism for the formation of the CaCO_3 /PMMA composite microspheres in a soapless emulsion polymerization process.¹⁸ Here, the primary goal is to investigate what is the key to

Correspondence to: Z. Wang. (wangzc@mail.jlu.edu.cn).

increase the amount of nanofillers in the inorganic/organic composites via the soapless emulsion polymerization.

EXPERIMENTAL

Materials

Calcium oxide (CaO) was of reagent grade, provided by Changzhou Menghe Chemicals factory. Methyl methacrylate (MMA) was analytical reagent and not distilled. Ammonium persulfate (APS) were used without further purification as an initiator. OA was analytical reagent and conserved at 4°C. SS was purchased from Guoyao Chemicals factory and without further purification. Distilled and deionized water was used throughout the work.

Pretreatment of nano-size CaCO₃ latex

Calcium carbonate nanoparticles were self-prepared with the carbonation process of Ca(OH)₂ slurry by CO₂. The temperature was an important factor to control the size distribution of CaCO₃ nanoparticles. The optimal condition of the temperature was under 15°C. The concentration of Ca(OH)₂ slurry was diluted to 0.35M and the flux of CO₂ was controlled under the 0.3 L/min.

A three-necked flask equipped with mechanical stirrer was charged with the above-mentioned nanometer CaCO₃. Then OA or SS was dropped into the flask. To achieve better dispersity in water, some ethanol was added into the OA beforehand and the SS was dissolved in 80°C deionized water. After 1-h vigorous stirring at 60°C, the hydrophobic CaCO₃ nanoparticles with mean size around 40 nm were obtained. Furthermore, all the CaCO₃ nanoparticles could float on the surface of water without further treatment.

The PMMA-modified CaCO₃ nanoparticles were prepared as follow: The MMA monomer was added into the nano-CaCO₃ latex. When the temperature reached to 80°C, APS were added into the system to initiate the polymerization of MMA. The pretreated process last 4 h with vigorous stirring as the process of modifying CaCO₃ with SS or OA. The amount of all modifying agents was constant, with 2 wt % of CaCO₃ nanoparticles.

Preparation of PMMA-CaCO₃ nanocomposites

A 500-mL four-necked flask equipped with thermometer, mechanical stirrer, reflux condenser, and N₂ inlet, was charged with deionized water and modified CaCO₃ (2.5 g) nanoparticles. APS (0.100 g), as an initiator, and MMA (5 mL) were added dropwise into the flask at 60°C. The mixture maintained

at this temperature for 0.5 h and then at 80°C for 4 h. The product was collected by suction filtration and then dried at 90°C for 6 h.

Characterization

FTIR spectra were recorded using a Shimadzu FTIR-8400S spectrometer on powder pressed KBr pellets. X-ray diffraction (XRD) patterns of products were performed on a Shimadzu XRD-6000 that filters Cu K α radiation. A Mettler Toledo 825^e instrument was applied to analyze the filler content and the thermal stability of the composites. The samples were heated from 50 to 600°C at 20°C/min in an air atmosphere. The contact angle was measured at 25°C with a FTA200 (USA) contact angle instrument. Field-emission scanning electron microscopy (FESEM) using a JEOL JSM-6700F electron microscope was used to determine the morphology of the products.

RESULTS AND DISCUSSION

Morphology of PMMA-CaCO₃ nanocomposites

Figure 1 showed the FESEM pictures of pure PMMA and PMMA-CaCO₃ composites. All the samples were diluted with deionized water, and then dipped onto the silicon slice. Before FESEM imaging, the samples were sputtered with thin layers of gold. It could be seen that both the pure PMMA and PMMA-CaCO₃ nanocomposites polymer particles were uniformity microspheres, as shown in Figure 1. The diameter of the composites polymer microspheres was bigger than that of the pure PMMA (150 nm). The diameters of the composites polymer were 420, 310, and 260 nm when the CaCO₃ nanoparticles were modified with SS, OA, and PMMA, respectively. In addition, the surface morphology of polymer microspheres was changed from slick to scraggy, when the nano-CaCO₃ particles were participated in the polymerization process. The phenomenon was probably contact to the unsymmetrical composite particles shrink when the nano-CaCO₃ particles were encapsulated in the PMMA matrix. The increase in the droplet size and the change of the polymer morphology suggested that the CaCO₃ nanoparticles were present in the emulsion droplets. In addition, some CaCO₃ nanoparticles could be seen on the surface of the PMMA composites when the CaCO₃ nanoparticles were pretreated by PMMA. On the contrary, within the CaCO₃ modified by SS and OA, no CaCO₃ nanoparticles were found in the whole visual threshold. As mentioned above, the conclusion could be presumed that the diameter of the composites polymer microspheres have a relation with the encapsulating ratios of nano-CaCO₃ in the

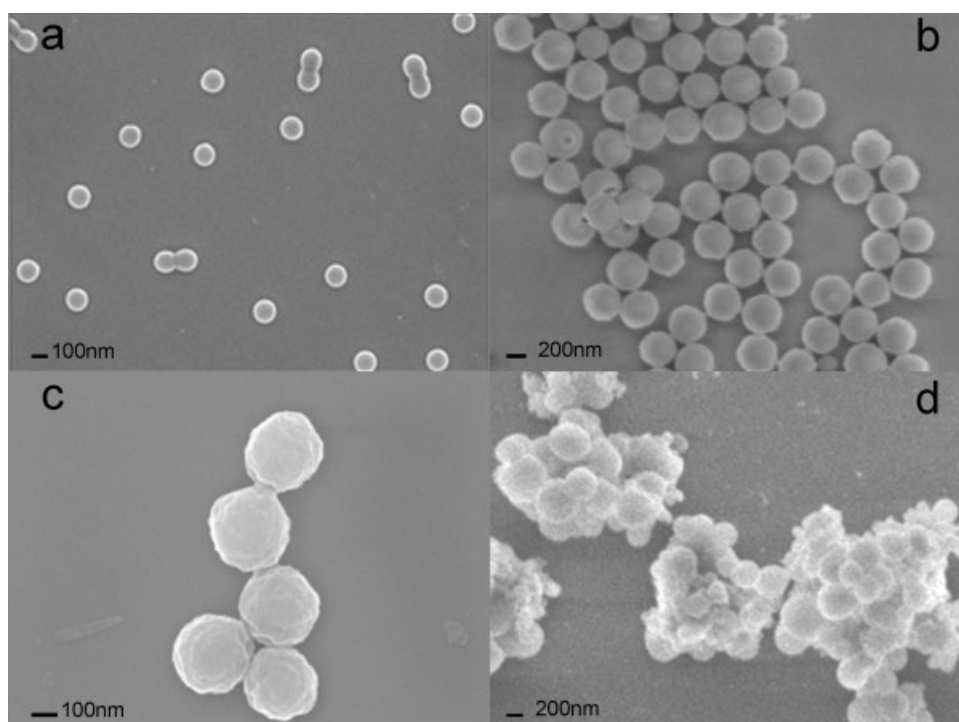


Figure 1 FESEM photographs of (a) pure PMMA microspheres; (b) composites prepared with SS-modified CaCO_3 ; (c) composites prepared with OA-modified CaCO_3 ; (d) composites prepared with PMMA-modified CaCO_3 .

composites and with the existent state of the CaCO_3 nanoparticles.

TGA of PMMA- CaCO_3 nanocomposites

The content of CaCO_3 nanoparticles within the PMMA- CaCO_3 composite microspheres can be analysed from the data of Thermo-Gravimetric analysis. By removing the unencapsulated CaCO_3 with 0.01M HCl solution before TGA testing, the amount of CaCO_3 in the composites could be regarded as the encapsulating ratio. The TGA plots of PMMA- CaCO_3 nanocomposites in which the CaCO_3 was modified by different modifying agents were shown in Figure 2. All of the samples were prepared under the same conditions as mentioned above. And the amount of nano- CaCO_3 added into the polymerization system was the same (50 wt %). The weight loss between 270 and 600°C in the composites can be used to calculate the amount of CaCO_3 in the composites. It could be seen in the plots that the PMMA- CaCO_3 nanocomposites displayed the notable difference in encapsulating ratio after CaCO_3 was modified with three modifying agents. The curves (a)-(c) in Figure 2 showed the TGA plots of the nanocomposites with the CaCO_3 nanoparticles were modified by SS, OA, and PMMA. According to the plots, the amounts of CaCO_3 in the composites could be calculated as 44.2, 28.3, and 7.8%, respectively. So the presumption in the above was proven by the result,

which is the more CaCO_3 -encapsulated in composites, the bigger diameter of composites obtained.

FTIR spectra of PMMA- CaCO_3 nanocomposites

The FTIR spectra of the PMMA- CaCO_3 nanocomposites prepared with SS, OA, and PMMA-modified nano- CaCO_3 were shown in Figure 3(a-c), respectively. The typical bands of PMMA were found at

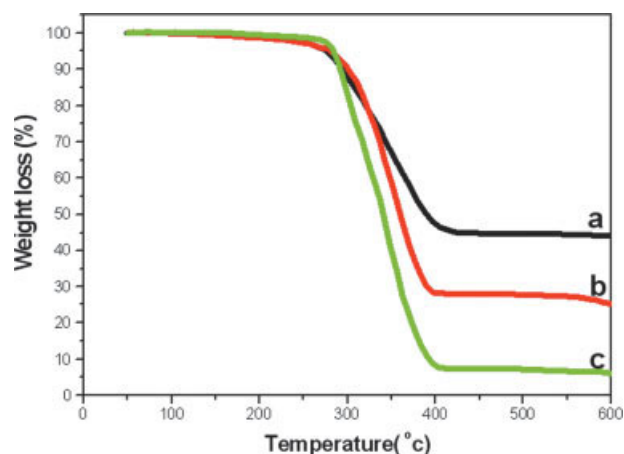


Figure 2 TGA plots of (a) composites prepared with SS-modified CaCO_3 ; (b) composites prepared with OA-modified CaCO_3 ; (c) composites prepared with PMMA-modified CaCO_3 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

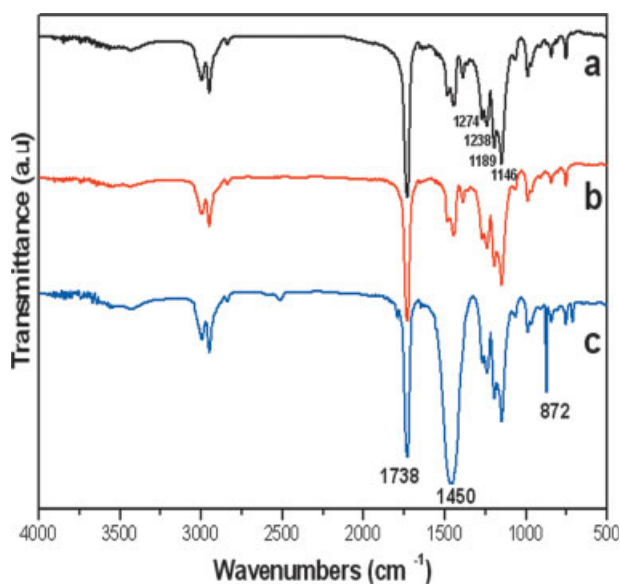


Figure 3 FTIR spectra of (a) composites prepared with SS-modified CaCO_3 ; (b) composites prepared with OA-modified CaCO_3 ; (c) composites prepared with PMMA-modified CaCO_3 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1738, 1146, 1189, 1274, and 1238 cm^{-1} in the IR spectra of all the composites. It was worth mentioning that the change of the peak at 1450, 872 cm^{-1} that come from the CO_3^{2-} of the nano- CaCO_3 particles. Without the obvious peak at 872 cm^{-1} in the curves (a) and (b), the specific adsorption peak of CO_3^{2-} at 1450 cm^{-1} was broadened due to the interaction between PMMA and CaCO_3 nanoparticles.^{19–21} On the contrary, the spectra of composites obtained with the PMMA-modified nano- CaCO_3 as shown in Figure 3(c) had a stronger specific adsorption peak of CO_3^{2-} . This was likely due to the adhesion of CaCO_3 nanoparticles on the surface of PMMA polymer microspheres. And the result was in good agreement with the conclusion derived from the FESEM.

XRD plots of PMMA- CaCO_3 nanocomposites

The presence of CaCO_3 nanoparticles in the PMMA- CaCO_3 nanocomposites was confirmed by XRD analysis, and the spectra were shown in Figure 4. First, the CaCO_3 crystal was calcite and did not change even after the polymerization as revealed by the results of XRD. Second, the intensity of the characteristic XRD peaks of the CaCO_3 nanofillers became different when the same amount CaCO_3 nanoparticles were added into the polymerization system. The difference between the composites prepared with SS-modified CaCO_3 (curve (a) in Fig. 4) and the composites obtained with OA-modified CaCO_3 (curve (b) in Fig. 4) could be attributed to the encapsulating ratios of nano- CaCO_3 particles in the com-

posites. However, the strongest intensity of XRD peaks was found in the composites prepared with PMMA-modified CaCO_3 nanoparticles (curve (c) in Fig. 4), which was likely due to the nano- CaCO_3 existing on the surface of the composites.

The surface state of CaCO_3 nanoparticles

The surface state of CaCO_3 nanoparticles after modification was evaluated by the contact angles. On the flat solid surface, the contact angle can be measured by the sessile drop technique. The sample was first pressed into a pellet then the water droplet was dropped onto the pellet. The contact angles of nano- CaCO_3 particles modified with SS, OA, and PMMA were listed in Figure 5(a-c), respectively. In Figure 5, the contact angle of the CaCO_3 modified by SS and OA were 125.96° and 111.30° . It was clearly that the surface state of them was hydrophobic. However, the contact angle of PMMA modified- CaCO_3 was 42.67° , which indicated that the surface of them was hydrophilic and it was easy to be wetted by water. As the results listed above, the conclusion could be presumed that the hydrophobic surface of CaCO_3 nanoparticles was a key to increase the encapsulating ratios of nano- CaCO_3 particles in the composites and to improve the compatibility between the CaCO_3 particles and MMA monomer in emulsion system.

CONCLUSION

In this work, PMMA- CaCO_3 composites microspheres were synthesized by soapless emulsion poly-

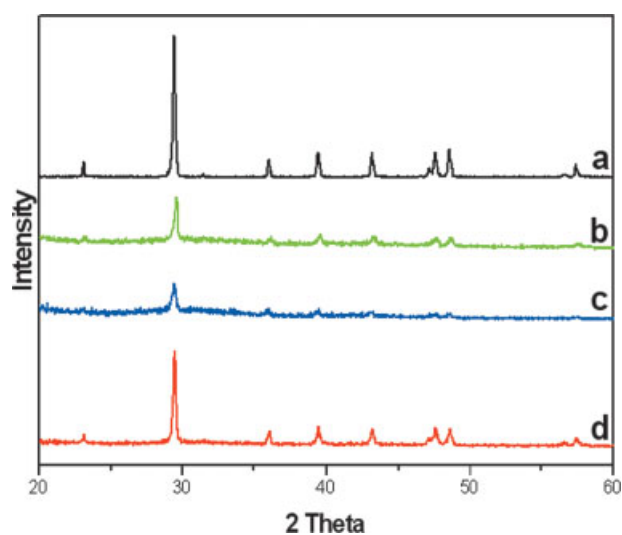


Figure 4 XRD plots of (a) CaCO_3 nanoparticles before polymerization; (b) composites prepared with SS-modified CaCO_3 ; (c) composites prepared with OA-modified CaCO_3 ; (d) composites prepared with PMMA-modified CaCO_3 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

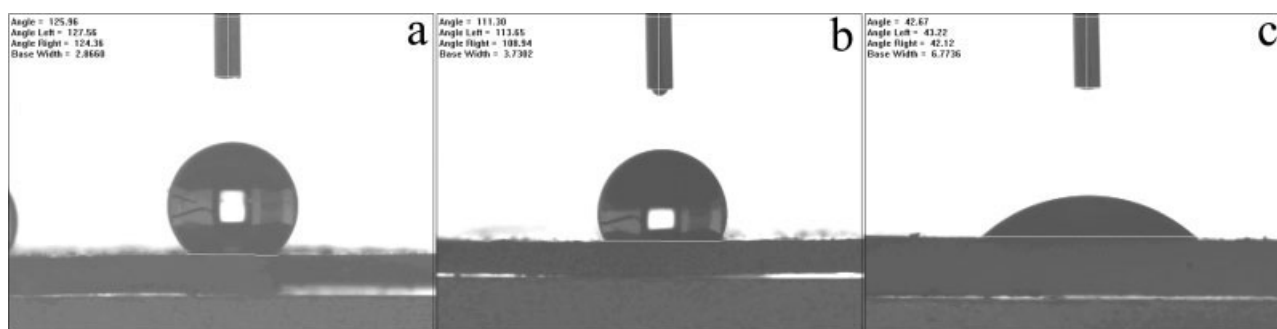


Figure 5 The contact angle of (a) SS-modified CaCO_3 nanoparticles; (b) OA-modified CaCO_3 nanoparticles; (c) PMMA-modified CaCO_3 nanoparticles.

merization after the CaCO_3 nanoparticles were modified with different modifying agents. Because of the good compatibility between the nanofillers and the polymeric matrix, the hydrophobic CaCO_3 pretreated by SS and OA could be well encapsulated into the PMMA organic matrix. However, the PMMA modified nano- CaCO_3 just displayed the good compatibility with the PMMA matrix and did not locate the CaCO_3 into the PMMA microspheres. In addition, the unsaturated $\text{C}=\text{C}$ chemical bond of OA did not increase the encapsulating ratio of CaCO_3 nanoparticles in the composites, either. It was likely due to the location of the unsaturated $\text{C}=\text{C}$ being in the central of the molecular structure. Sum up, the hydrophobic property was a key to increase the encapsulating ratios of nano- CaCO_3 particles in the composites and to improve the compatibility between the CaCO_3 particles and MMA monomer in such a soapless emulsion system.

References

- Loiseau, J.; DoeIrr, N.; Suau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladavière, C. *Macromolecules* 2003, 36, 3066.
- Renger, C. J.; Burrows, S. J.; Shanks, R. A. *J Appl Polym Sci* 2001, 82, 3091.
- Leea, C. F.; Youngb, T. H.; Huangc, Y. H.; Chiuc, W. Y. *Polymer* 2000, 41, 8565.
- Yu, D. G.; An, J. H. *Polymer* 2004, 45, 4761.
- Yeh, J. M.; Weng, C. J.; Liao, W. J.; Mau, Y. W. *Surf Coat Technol* 2006, 201, 1788.
- Althues, H.; Palkovits, R.; Rumpelcker, A.; Simon, P.; Sigle, W.; Bredol, M.; Kynast, U.; Kaskel, S. *Chem Mater* 2006, 18, 1068.
- Meneghetti, P.; Qutubuddin, S. *Langmuir* 2004, 20, 3424.
- Wang, Z.; Xie, G.; Wang, X.; Li, G.; Zhang, Z. *Mater Lett* 2006, 60, 1035.
- Naka, K.; Tanaka, Y.; Chujo, Y. *Langmuir* 2002, 18, 3655.
- Balz, M.; Barriau, E.; Istratov, V.; Frey, H.; Tremel, W. *Langmuir* 2005, 21, 3987.
- Donners, J. J. M.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *J Am Chem Soc* 2002, 124, 9700.
- Shen, Q.; Chen, Y.; Wei, H.; Zhao, Y.; Wang, D.; Xu, D. *Cryst Growth Des* 2005, 5, 1387.
- Yang, Y.; Kong, X. Z.; Kan, C. Y.; Sun, C. G. *Polym Adv Technol* 1999, 10, 54.
- Yu, J.; Yu, J.; Guo, Z.; Gao, Y. *Macromol Rapid Commun* 2001, 22, 1261.
- Avella, M.; Errico, M. E.; Martuscelli, E. *Nano Lett* 2001, 1, 213.
- Wu, W.; He, T.; Chen, J.; Zhang, X.; Chen, Y. *Mater Lett* 2006, 60, 2410.
- Chen, N.; Wan, C.; Zhang, Y.; Zhang, Y.; Zhang, C. *J Appl Polym Sci* 2005, 95, 953.
- Ma, X.; Zhou, B.; Sheng, Y.; Wang, C.; Pan, Y.; Ma, S.; Gao, Y.; Wang, Z. *J Appl Polym Sci* 2007, 105, 2925.
- Li, Z.; Zhang, J.; Du, J.; Mu, T.; Liu, Z.; Chen, J.; Han, B. *J Appl Polym Sci* 2004, 94, 1643.
- Li, Z.; Zhu, Y. *Appl Surf Sci* 2003, 211, 315.
- Sheng, Y.; Zhou, B.; Wang, C.; Zhao, X.; Deng, Y.; Wang, Z. *Appl Surf Sci* 2006, 253, 1983.