Double-Shell Surface Modifications of Large Poly(methyl methacrylate) Spheres

Weihong Guo,[1] Yvon G. Durant,[2] Jikui Wang,[1] Chifei Wu[1]

[1]Polymer Alloy Research Group, Department of Materials Science and Engineering, East China University of Science and Technology. Shanghai, 200237, People's Republic of China
[2]Advanced Polymer Lab, University of New Hampshire, Durham, NH 03824

ABSTRACT: Two reactive shells were polymerized on poly(methyl methacrylate) (PMMA) spheres to improve the compatibility of the spheres with a paint binder. By adjusting the buoyancy of the polymerization medium, PMMA, retroreflective spheres with an average diameter of 600 μm were successfully modified with a thin cross-linked layer together with an amine functional layer outside on the surface. The cross-linked layer was polymerized by methyl methacrylate and ethylene glycol dimethacrylate by suspension polymerization. After that, a second monomer with functional amine group was polymerized and a functional layer was formed on the surface. The amine groups on the modified spheres can react with the enamine groups of acetoacetate already formulated in the binder and connected the spheres and the paint by chemical bond. The structure of the modified spheres was studied using transmission election microscopy, FTIR, DSC, and other tests.© 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 829–836, 2005

Key words: surface modification; large spheres; crosslink; enamine

INTRODUCTION

Generally, glass retroreflective beads are used to reflect light on the highway for safety. Glass beads are mechanically projected on freshly applied paint film to provide the light reflection that is essential for night driving. The beads are significantly larger than the thickness of the paint film, which ensures that the spheres are raised above the film. The adhesion of the spheres to the film is important and is usually described as bead retention. These spheres are typically made of glass and are surface modified and hence "compatible" with traffic paints. Typically they are projected on the surface of the wet paint and remain on top of the final coating. The interaction between coating and spheres is minimal and limited to surface adherence. Because of strong surface shear caused by traffic, spheres are sheared off the coating rapidly, within a few months and sometimes faster. Winter conditions and rapid change of temperature are even more stressful on the sphere–coating association since they have different thermal expansion coefficients. This research work deals with a specific aspect of traffic paint: improving the retention of retroreflective spheres. More specifically, we are studying the potential of poly(methyl methacrylate) (PMMA) spheres to

act as a substitute to glass spheres when their surface is modified to react (crosslink) with the binder.[1–6] An alternative to glass spheres is impact-modified PMMA spheres. They can be strong enough to endure the compression shocks of road traffic. Polymer spheres have a thermal expansion coefficient that is nearly equal to that of the traffic paints. Consequently, the stress of thermal expansion between the binder and the surface would be lower.[7–10] Polyenemines can be made from the reaction of polyacetoacetates or poly-acetoacetamides with polyamines by mixing the compounds together in the proper proportions. Because there are acetoacetate functional groups contained in the binder of the traffic paint, the retroreflective spheres can be modified with amine groups on the surface. Preparation of polymers containing functional amine groups and then following the reaction with a functional acetoacetate to form an enamine structure has many uses including coatings, sealants, adhesives, and saturant applications and are most useful as solutions or dispersions in water or water–cosolvent mixtures.[10,11]

The strategy involves the addition of a PMMA cross-linked shell together with a grafted functional shell at the surface of the beads. Two methods were used for the modifications:

(1) An amine group content monomer was polymerized on the surface of the spheres after the spheres were crosslinked by the polymerization of methyl methacrylate (MMA) and ethylene glycol dimethacry-

late (EGDMA); the amine content monomer can be methacrylamide (MAA) or acrylamide (AA).

(2) The spheres were crosslinked by MMA and EGDMA as method one, after step one, 4-vinylbenzyl chloride (VBC), was polymerized on the surface of the spheres, and the spheres were treated with $NH_3.H_2O$. The schematics of the modifications and the reaction of the binder with the modified beads are shown in Figure 1.

EXPERIMENTAL

Materials

MMA (Acros Organics), VBC (Acros Organics), MAA, AA, and 4-aminostyrene (AS) were used as monomers. Inhibitors were removed from these monomers by alumina absorption. We used 2, 2′-azo-bis(2-methylpropionitrile) (AIBN, Acros Organics) as initiator. Sodium dodecyl sulfate (SDS, Acros Organics) was used as surfactant. Other chemicals were used as received.

The traffic paint, Primal Fastrack HD-21A, was manufactured by Rohm and Hass Co. The MG102 Clear 011. Diakon acrylic bead polymer from Ineos Acrylics was chosen as the original spheres.

Characterization

A Nicolet 205 FTIR spectrometer was used to analyze the chemical structure of the binder. The particle size and the distribution of the beads were tested by a Microtrac S3000 particle size analyzer. Centrifuge filter devices from Millpore Corp. were used to test the solid content of the aqueous solution.

Infrared analysis of the modified polymers was performed with a Nicolet 205 FTIR spectrometer. TEM sections were done on a Boeckeler RMC MT XL Ultramicrotome. A Diatome 35° diamond knife was used to cut the sections. Grids subsequently were stained with ruthenium tetroxide vapors for 10 min. Samples were tested in a Jeol 100S TEM and negatives were taken.

The transparency of spheres was determined by a UV-visible spectrophotometer (Cary 400 UV). A rectangular demountable cell with one open face was used for the transparency test. The scan was performed from 400 to 800 nm, which corresponded to the visible light spectra range. Thermal properties were measured under nitrogen in a Perkin–Elmer-7 differential scanning calorimeter on a chip of about 5 mg. The thermal program included a hold for 3.0 min at −50.00°C, followed by a temperature scan from −50 to 140°C at a rate of 20.00°C/min.

Experiments

Modifications were carried out in a 1-L jacketed reactor with mechanical stirring, condenser, nitrogen flow, and a thermocouple. Different feed strategies, solid content, reactor temperature, monomer, and different concentration of the continuous aqueous phase were used.

Suspension polymerization steps were carried out for each reaction. First, dodecyl sulfate sodium salt (SDS) and initiator (AIBN), together with the density adjuster (sucrose), were solved in water and added in the reactor. After the stirwas begun, unmodified PMMA spheres were dropped into the reactor. When the temperature was stabilized at 60°C, the two monomer feeding pumps were started. The first pump feeds in the monomer and the second one feeds in a solution of initiator and sucrose.

Monomers were fed in by two sequences. Monomer 1 is a mix of MMA and EGDMA as a cross-link agent, while the second sequence contained one of the following amine groups, such as AA, MAA, or VBC. The first sequence aimed at creating a shell layer on the PMMA core bead that is particularly strong and resistant to solvent and oil, while the second shell layer provide the network structure of an amine functional water soluble polymer. This final layer is there to react with the binder upon application.

The feed-in time was 1 h for each group of monomers. The pump for the initiator was adjusted at a speed so as to end the initiator 40 min after monomer 2. The reaction was maintained for about 3 h. Thirty minutes after the initiator finished, heat was stopped and stir was continued. While the reactor cooled down to room temperature, stirring stopped, and the spheres and the solution were put out. A testing sieve was used to separate the spheres and the solution. The spheres were washed with water three times and then spheres were dried in an oven at 60°C. The monomer VBC was polymerized using the second step as the first polymerization and then the spheres were treated with $NH_3.H_2O$.

RESULTS AND DISCUSSION

Raw materials

According to standard specification for glass spheres used in traffic paint,[12] the spheres should be transparent, clean, colorless, smooth and spherically shaped, and free from milkiness, pits, or excessive air bubbles. Additionally, they should conform to the following requirements: The spheres should have a minimum of 70% true sphere, remain free of clusters and lumps, and flow freely from the dispensing equipment. The spheres should have a diameter between 0.45 and 0.85 mm. After comparing different kinds of PMMA spheres, the MG102 clear 011 Diakon acrylic bead polymer from Ineos Acrylics was chosen as the original spheres. The particle size and the distribution of PMMA spheres were measured and they have an average diameter of 686.7 μm.
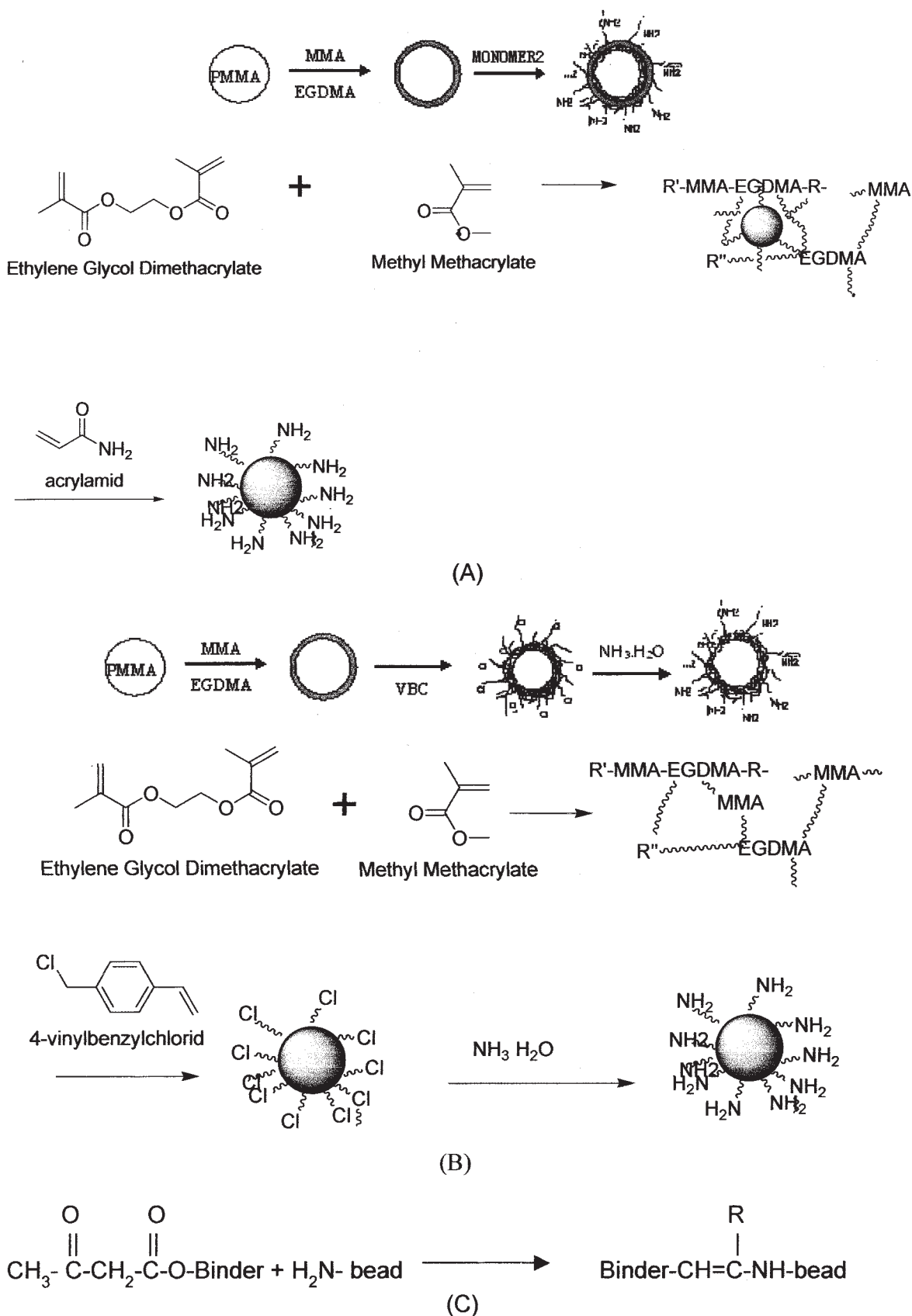
Figure 1 (A) Schematic of method 1: the "double shell" approach to producing the modified spheres by amine contained monomer. (B) Schematic of method 2: the "double shell" approach to producing the modified spheres by VBC. (C) Reaction of the modified beads with the binder.[15–18]

TABLE I
Effect of Sucrose Amount to the Yield of the Reaction

Sucrose (%)	0	40	45	50
Yield of the reaction (%)	45.6	65.3	66.7	58.9

The selected traffic paint, Primal Fastrack HD-21A, manufactured by Rohm and Hass Co., has a solids content of 49.0% and a viscosity of 38 cP, and a pH of 10 and especially has an acetoacetate reactive functional group.[13] One milliliter of the latex was placed in a petri dish and dryied in a vacuum oven at 80°C for 48 h. This sample was analyzed by infrared (IR) spectroscopy. In a second analysis 2 mL of 1.0 M HCl was added to 10 mL HD21A latex to separate the latex from the fillers. The deposit was washed with water three times until the pH became stable at 7.5. The deposit was dried in a vacuum oven at 80°C for 48 h. In both IR spectra there are broad peaks at 2200–2650 cm^{-1} related to the vibration of –C = N/-N-C = O. Acetoacetate groups react with functional amine to form enamines. Consequently, we will modify the polymer beads with functional amine to connect the binder and the beads together. For the thermal program, the dried membrane glass transition (T_g) was measured to be 16°C, and the T_g of the deposit was 24°C.

Density adjustments

To obtain neutral buoyancy of the PMMA beads, the density of the aqueous solution had to be refined. We adapted some of the findings of U.S. Patent 5447983 with the general formula[11]

$$\rho_B - 0.03 < \rho_A < \rho_B + 0.03,$$

where ρ_A is the specific gravity of the organic phase (bead), and ρ_B is the specific gravity of the aqueous phase. Sucrose was used to adjust the density of the aqueous phase. The density of PMMA is 1.19 g/cm^3, which implies $\rho_B - 0.03 < 1.19 < \rho_B + 0.03$. ρ_B should be in the range of 1.16–1.22 g/cm^3, and the concentration of sucrose should be in the range of 38 to 50%.[14] Different densities of the aqueous phase for PMMA beads were tested and the best concentration of sucrose for our system was 40%. In such a solution, the beads can disperse effectively from the beginning to the end of the reaction. Samples of aqueous phase were taken out of the reactor as function of time to test the density and the density remains practically constant through the duration of the reaction. The effect of sucrose to the yield of the reaction is shown in Table I. The yield of the reaction is

$$\frac{\text{(Weight of modified PMMA} - \text{Weight of unmodified PMMA)}}{\text{(Weight of all monomers added in)}}$$

In reactions with no sucrose in the aqueous phase, the PMMA spheres sank at the bottom of the reactor and only flowed by stirring. As the reaction continued, the spheres connected and large bulks of PMMA were formed. When sucrose was added, the spheres dispersed much better in the aqueous phase and a larger surface area was available for the reaction. Less big bulks were formed, and much more monomer could be dispersed on the surface of the PMMA spheres and polymerized on the surface of the spheres. Also, in reactions with no sucrose, the stirring speed must be
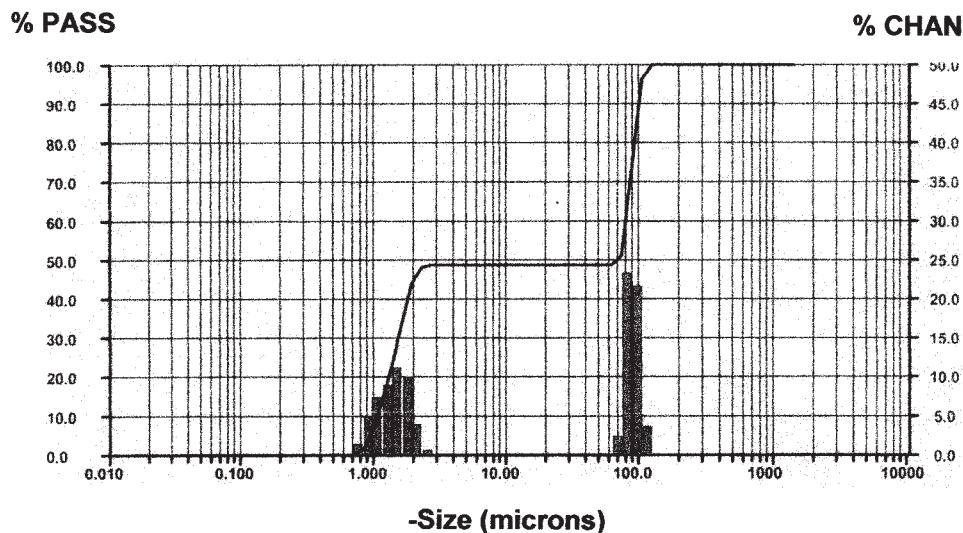

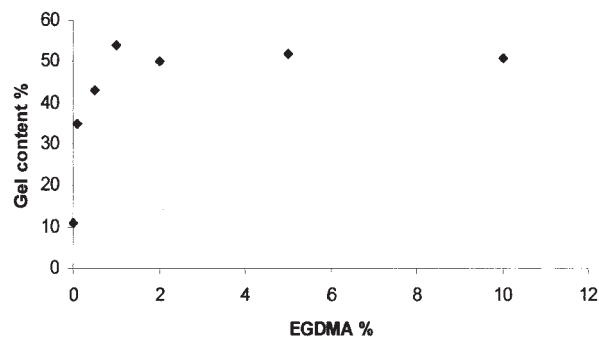**Figure 2** Analysis of the aqueous phase solution after the reaction.

Figure 3 Effect of the amount of EGDMA added to the gel content.

Figure 4 Transparency of the modified spheres, initial polymer spheres, and glass spheres.

kept at a higher speed to flow the spheres in the middle of the aqueous phase. At a relative higher stirring speed, the spheres had a much higher momentum, and when the collisions occurred, many more spheres connected. By adding sucrose, the spheres flowed and the adjustment of the stirring speed became possible. We could set the stirring speed at a relatively lower speed that was enough to move the spheres, but they moved slowly with much less momentum. Because the PMMA spheres are fairly large, the higher stirring speed provided excessive momentum to the spheres and increased agglomeration. Monomer feed strategies were also experienced with feed from the top of the reactor; feed in the middle of the reactor; and feed with some sucrose solution as an emulsifier; no significant changes were detected in the final product for each technique.

Aqueous phase analysis

To ensure that the polymerization happened on the surface of the spheres, the aqueous phase after the reaction was analyzed (spheres were put out). The solution was filtered using filter paper and washed with distilled water 3 times. Then the paper was dried in a vacuum oven at 50°C and the remaining monomer left was removed. The weight difference of the paper before useg and after drying was the solid content in the solution (not solved in water). The results show that the solid content of the aqueous phase following the reaction was less than 0.5% of the weight of the monomer, which means little of the monomer was self-polymerized; most of the monomer was polymerized on the surface of the solid beads. Evidence from the centrifuge filter also shows the same result. The solution was centrifuged in a Microcon centrifugal filter device. Then the filter was filled with distilled water and centrifuged 3 times. After the filter was dried, the solid content in the solution was calculated to be less than 0.5% of the total weight of monomer. The particle size in the solution under "wet conditions" is shown in Figure 2. The particles contained in
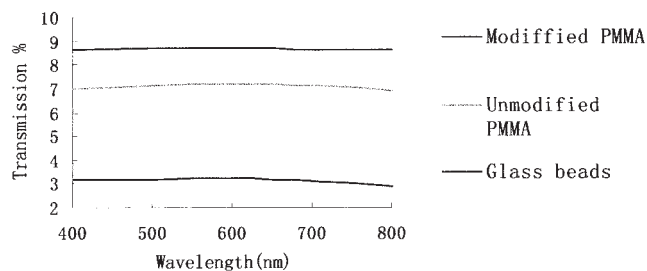
the aqueous phase had a diameter of 87.9 (51%) and 1.1 μm (49%). The particles were almost all the monomer cells that did not react in the polymerization because the solid content in the aqueous phase was less than 1% of the monomer.

Crosslink

The amount of crosslinked proportion was tested by solvent extraction. Modified spheres and initial PMMA spheres were placed into filter bags. Extraction with a solution of tetrahydrofuran was performed for 48 h. After the bags were dried, their contents were weighed. The gel content of the modified spheres was 54%, while that of the unmodified PMMA was 11%. Consequently, the modified spheres are clearly crosslinked on the surface while the unmodified spheres have little to no crosslinker. The effect of adding different amounts of EGDMA to the gel content is shown in Figure 3. The gel contents increased with an increase in EGDMA. Even 0.1% content of EGDMA can make the crosslink, and 1–2% EGDMA is enough to form a good crosslink outside surface layer.

Particle size and transparency

Modified spheres were tested and the average diameters in different matches of the modified spheres ranged from 784.7 to 912.3 μm. All modified PMMA spheres are larger than the initial spheres, with a significantly narrower size distribution.
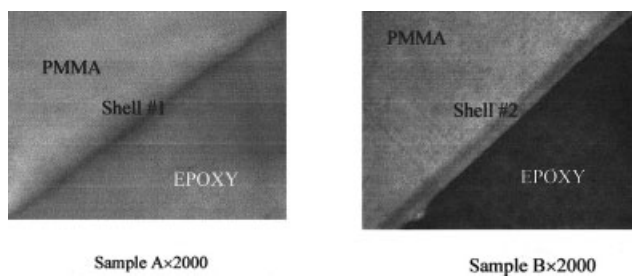

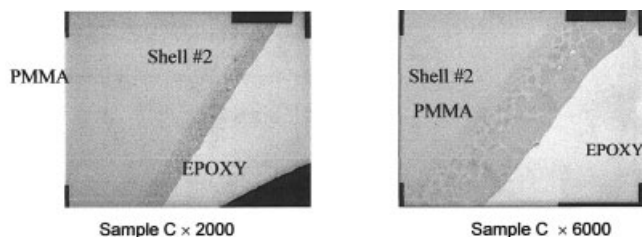**Figure 5** TEM images of samples magnified 2000×.

Figure 6　TEM images of the VBC modified spheres.

The results of the UV test are shown in Figure 4. The modified spheres had the highest transparency and the initial PMMA spheres were in the middle. Both had higher transparency than the glass spheres.

Transmission electron microscopy characterization

To confirm the expected double-shell structure of the modified spheres, a specific staining technique that involves reacting our samples with RuO_4 vapors was conducted. This oxide reacts only with aromatic chem-ical groups such as the ones present in benzyl acrylate (BzA), AS, and VBC. Samples were prepared by first microtoming the modified PMMA spheres embedded in epoxy and then staining the samples with RuO_4.

Sample A had only a single step of comonomer addition using MMA, EGDMA, and BzA. Sample B was modified using a two-step addition process, including some BzA in the second step to see the second shell layer. Sample C was also modified using a two-step addition process, including VBC in the second step, which shows the second shell layer. The benzyl groups that were added in VBC could be stained to a dark color, and the outside edge of the section should be a dark ring.

TEM showed an obviously stained ring around the transparent PMMA. The thickness of the stained layer was 5–8 μm.

From these TEM images (Figures 5 and 6), we concluded that we were successful at controlling the morphology of our spheres, imposing a core-shell-shell structure, and maximizing the presence of the functional monomer to the surface of the bead.
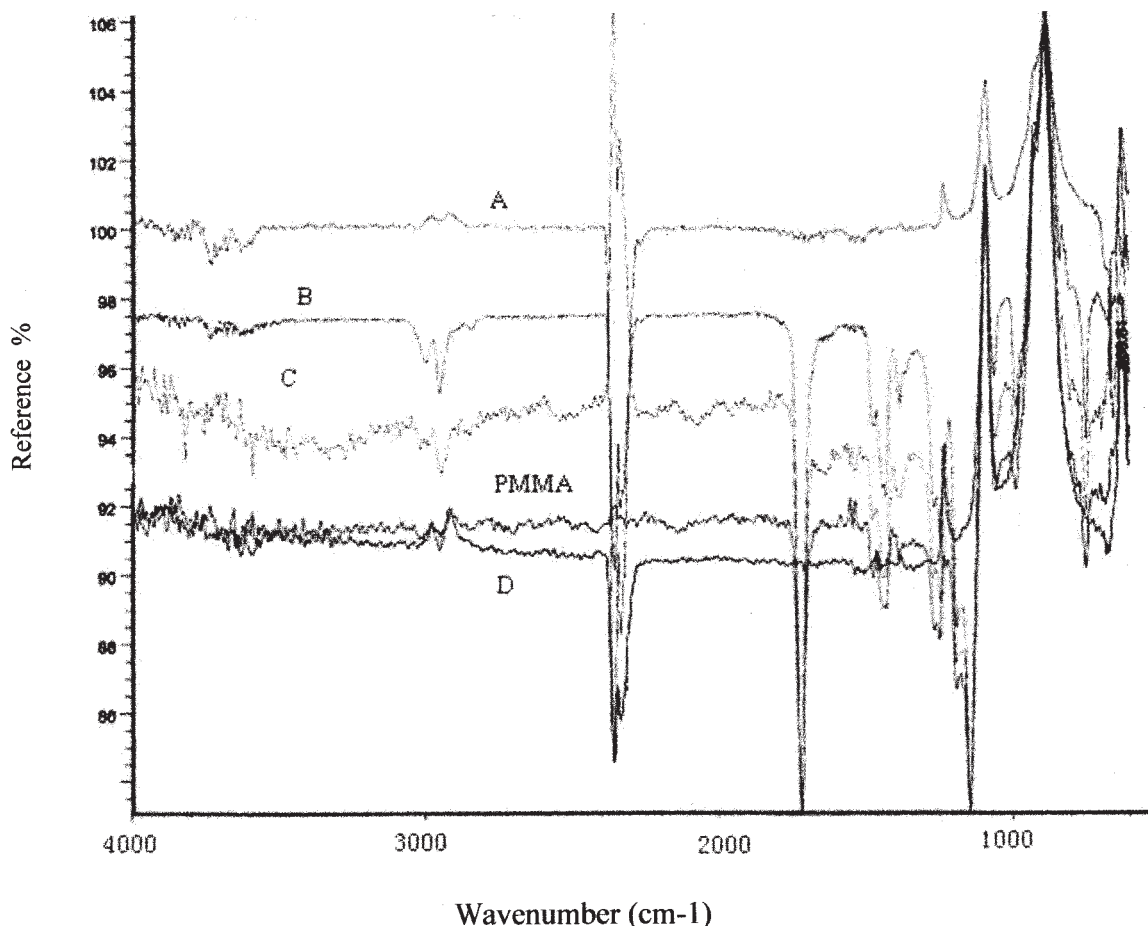

Figure 7　FTIR traces of modified spheres with ATR probe. A: The second monomer is VBC + EGDMA. B: The second monomer is AA + EGDMA. C: The second monomer is MAA + EGDMA. D: The second monomer is VBC + MMA + EGDMA and treated with $NH_3 \cdot H_2O$.

TABLE II
FITR Spectra Analysis

Sample	Monomer in synthesis	Peak @ 1730 cm^{-1}	Peak @ 2400 cm^{-1}	Peak @ 2900 cm^{-1}	Confirmation of surface function
A	VBC	No	Yes	Yes	Amine
B	AA	Yes	Yes	Yes	Amide
C	AAM	Yes	yes	Yes	Amide
PMMA	—	Yes	No	No	Acrylate
D	VBC	No	yes	Yes	Amine

FTIR analysis

Infrared spectrometry was the most suitable method for determining the modified surface. The analysis was performed with Fourier transform infrared spectrometry (Thermo Nicolet/Avatar 360 FTIR ESP). This FTIR setup is particularly sensitive to the chemical functions available at the surface of the spheres and is insensitive to the bulk characteristic of the spheres. The results are shown in Figure 7 and the list of the peaks is shown in Table II.

At 1730 cm^{-1}, the vibration is typical of carbonyls, present in acrylates (PMMA) and acrylamides. The vibration at 2400 and 2900 cm^{-1} is typical of $=$NH present in amines and amides, but with a higher response to amides at 2900 cm^{-1} than for amines. The peak at 2700–2250 cm^{-1} shows the movement of $=$NH$_2^+$ and $=$NH$^+$ together. The peak at 1650–1560 cm^{-1}, indicates the movements of –NH$_2$. In all the different monomer samples, we can find the trail of amine. By using VBC as the monomer, we can gain the largest yield percentage, which indicates that most of the monomer was polymerized on the spheres. With this information we are able to conclude that the chemical functions that we aim at introducing at the surface of the spheres are effectively present. This is valid for both amides and amines. This directly correlates with and reinforces the results of TEM.

Road test

Figure 8 shows the relationships between relative retroreflectivity and the applied time. This location offers mild winter conditions with plowing. The samples were located in the direction of the traffic, one set in the right wheel track with high wear and the other outside of the traffic, in the breakdown lane with low wear. From Figure 8, we can see that the modified PMMA beads have a better relative retroreflectivity than the glass beads under high wear conditions after the beads had been applied about 200 days. Farther applications can be seen at http://www.unh.edu/apl/RR-traffic-coating.htm. The modified PMMA beads can be used for 18 months and the life span is longer than that of the glass beads, which can be used about 6 months.

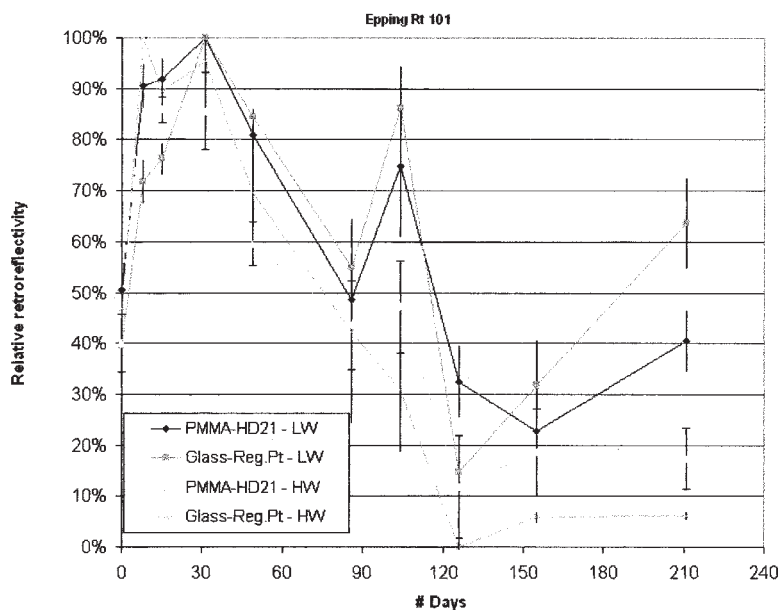**Figure 8** Relative retroreflectivities of the modified beads and glass beads with high wear (HW) and low wear (LW).

CONCLUSIONS

This study gives an original approach to modify large polymer spheres by adjusting the buoyancy of the polymerization medium. This method can also be used to functionalize other surfaces such as flat surfaces. This work shows the interesting polymerization site of the monomer. The results show that the monomer polymerized on the spheres and not self-homopolymerized to form small particles under suspension conditions. The double-shell structure was formed, and together the spheres were crosslinked and functionalized on the surfaces. Moreover, 1 wt % content of EGDMA can make the surface crosslinkage. The outside amine layer can also provide excellent reaction activities of the surface. This type of approach should be successful for coatings, sealants, adhesives, and saturant applications and is most useful as solutions or dispersions in water or water–cosolvent mixtures.

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