Experimental Investigations of Polypropylene and Poly(vinyl chloride) Composites Filled with Plerospheres

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ABSTRACT: Plerospheres, defined here as superfine spherical particles (0.5–5 μm) separated from fly ash (rather than as other solid spherical particles, as some have used the term), are separated from coal fly ash but are dramatically different from it. Plerospheres can be used as polymer fillers to improve the properties of composites. With plerospheres used as fillers for polypropylene (PP) and unplasticized poly(vinyl chloride) (UPVC), the effects of the filler content, the particle sizes of the plerospheres, and the coupling agent on the composite properties were studied. The particle sizes of the plerospheres were 2 and 5 μm. The results suggested that the notched impact properties both at a normal temperature and a low temperature and the tensile and flexural properties of plerosphere/PP increased significantly when the content was increased from 0 to 30 wt % and further increased with the addition of a coupling agent. Differential scanning calorimetry indicated that the thermal properties of the plerosphere/PP composite improved. The surface characteristics and morphology of the impact fracture surface were examined in detail with scanning electron microscopy. The rheological performance of plerosphere/UPVC pipe composites obviously improved; the plasticizing time was shortened, and the maximum torque was reduced. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 126–131, 2004

Key words: poly(propylene) (PP); poly(vinyl chloride) (PVC); composites; mechanical properties

INTRODUCTION

Coal fly ash, an industrial solid-waste byproduct, is produced in large quantities during the combustion of coal by thermal power plants. Thousands of millions of tons of fly ash are generated in the world each year. A huge source of pollution, fly ash can also be a huge resource. The storage and disposal of coal fly ash, designed to avoid environmental pollution, have become a worldwide problem, and the reuse of fly ash is becoming increasingly important. During the last few decades, the wide use of fly ash has been studied by many researchers, and fly ash has been used in many areas, such as cement and concrete applications, brick, ceramic tile, light-weight aggregates, highway pavement, road bases, subgrades, and backfills.[1–3] Most of these are low-added-value uses. Recently, many researchers have used fly ash as a filler for plastics, paints, insulating materials, and metal matrix composites and have made beneficial use of fly ash.[1,4–8]

There are many superfine spherical particles in coal fly ash; these are called *plerospheres*. Plerospheres are formed during the burning of coal at 1500–1800°C. When molten incombustible minerals in coal pass through a flue, many plerospheres are formed under the conditions of turbulence, surface tension, and emergency cooling. The main components of plerospheres (80–90%) are silicon dioxide (SiO_2) and alumina (Al_2O_3). The mineralogical compositions found by X-ray diffraction analysis are mullite, sillmanite, and quartz. The surface Mohs' hardness of plerospheres is 6–8. Plerospheres also possess many other excellent characteristics, such as sphericity, high strength, high resistivity, and low thermal conductivity. By air classification, a large quantity of plerospheres can be obtained with a diameter ranging from 0.5 to 5 μm. Plerospheres are dramatically different from coal fly ash. One of the most important uses of plerospheres is as fillers for plastic products. Nowadays, mineral fillers are widely used in plastic products to improve the performance and to reduce the costs. More than 17% of plastic products contain mineral fillers. Sometimes, the addition of mineral fillers may lead to a reduction of the impact strength.[9,10] Plerospheres represent a potential replacement for these mineral fillers and may improve both the strength and toughness of plastic products. They may have more advantages than traditional fillers.

Polymers filled with fly ash have been investigated by a numbers of researchers,[2,7,8,11] but so far, not much work has been reported on the use of plerospheres as fillers for polymers. Chand[7] introduced fly ash into a thermosetting polyester and found that the impact strength and ultimate tensile strength decreased with

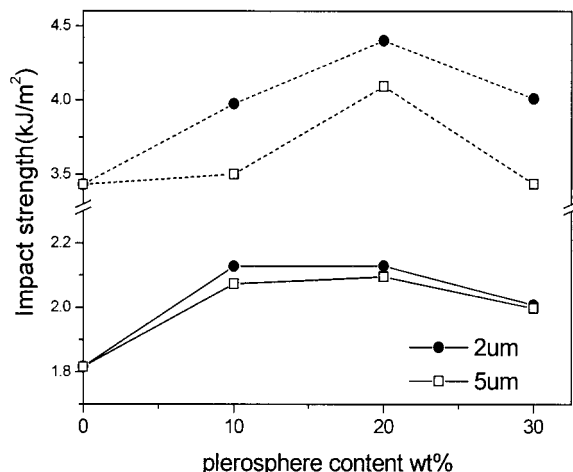*Correspondence to:* Z. Shen (szg@buaapowder.net.cn).

Figure 1 Notched impact strength of PP composites with the addition of modified plerospheres at (- - - -) 20 and (—) −20°C.

the addition of fly ash. Srivastava and Shembekar[11] also observed a reduction in the tensile strength when fly ash was added to an epoxy resin, but this was accompanied by an increase in the modulus and an increase in the fracture toughness with higher additions. Wong and Truss[8] studied fly-ash-filled polypropylene (PP) and found that the modulus of the PP composite increased, the yield strength did not change, and the impact strength decreased with the addition of the filler. In their studies, the filler was normal fly ash that was not well separated. Therefore, the particle sizes were not even, and there were many coarse particles in the fly ash material, even many irregularly shaped impurities. All of these could have led to the reduction of the mechanical properties. However, plerospheres are separated from fly ash by
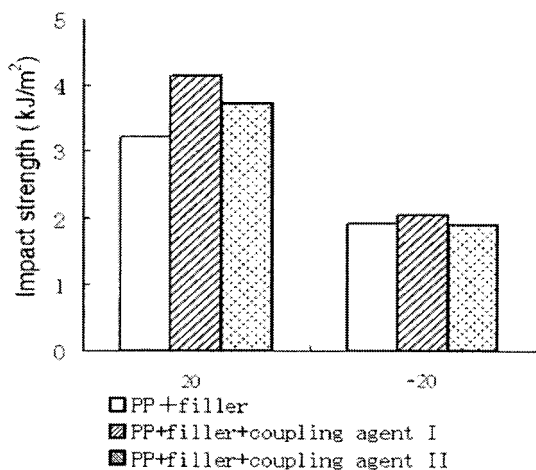

Figure 2 Effects of the coupling agent on the notched impact strength of plerosphere/PP composites. The filler content was 20 wt %.
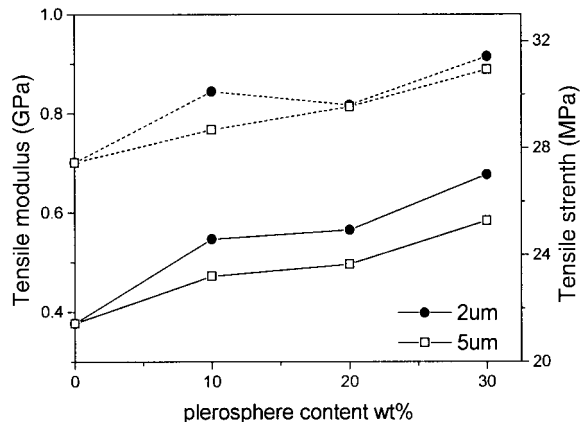

Figure 3 (- - - -) Tensile strength and (—) tensile modulus of PP composites with the addition of modified plerospheres.

air classification and should behave differently than fly ash. Therefore, plerospheres may produce better results. There are currently no reports on plerosphere-filled polymer composites.

Many researchers have also studied filled PP composites, and numerous fillers, such as talc, calcium carbonate, silica, and various other minerals, are used commercially. These fillers are added to increase the modulus of PP but are generally believed to reduce the toughness of composites.[8] In this study, plerospheres were used as fillers for two polymers, PP and unplasticized poly(vinyl chloride) (UPVC). The mechanical and thermal properties of the PP composites and the rheological behavior of UPVC were experimentally studied. The effects of the filler content, the particle size of the plerospheres, and the coupling agent on the mechanical and thermal properties were also studied.

EXPERIMENTAL

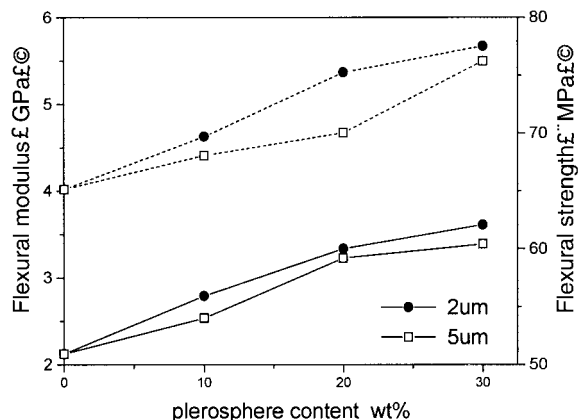The main materials used in this investigation were plerosphere, PP, and UPVC powders. The plerosphere

Figure 4 (- - - -) Flexural strength and (—) flexural modulus of PP composites with the addition of modified plerospheres.
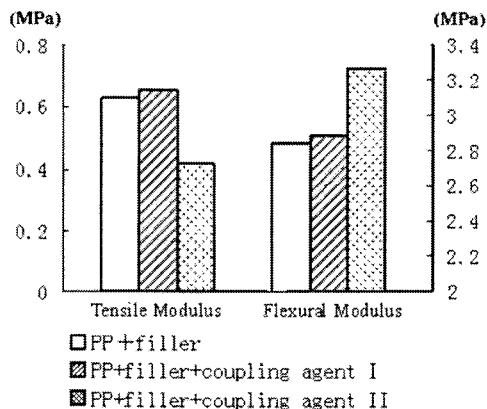
Figure 5 Effects of the coupling agent on the tensile modulus and flexural modulus of plerosphere/PP composites. The filler content was 20 wt %.

particle sizes were 2 and 5 μm, and the plerospheres mainly consisted of 56% SiO_2 and 31% Al_2O_3. The coupling agent was silane.

The plerospheres in this study were separated from coal fly ash by air classification, which was carried out by impeller centrifugal airflow classification. Before filling the polymers, the plerospheres were modified with the coupling agent by the aerosol method as follows. First, the plerospheres were dispersed, and the coupling agent was atomized by the airflow. Then, the atomized coupling agent and the dispersed particles combined to form an aerosol. The temperature of the system was controlled and maintained for a few minutes, and the modification of the filler was completed. The modification improved the compatibility between the plerospheres and the matrix. The selection of the coupling agent was very important for the composites. First, the plerospheres were mainly composed of SiO_2 and Al_2O_3. Under the action of air, many Si—OH bonds were generated on the surfaces of the plerospheres. The Si—OH bonds showed a strong trend of forming new chemical bonds (Si—O—Si) with a silane. Therefore, a silane was one of the best choices for the coupling agent. Second, the coupling agent needed to combine with the inorganic powder by its polar functional group; meanwhile, it had to combine with the organic matrix by its nonpolar functional group. Because every polymer matrix had a different polarity, a silane as a coupling agent had to meet the polarity requirement. For example, if the matrix was PP, silane A151 (triethoxy vinylsilane) was the proper coupling agent because the polarity of PP was very weak. If the matrix was poly(vinyl chloride) (PVC), silane KH-550 (γ-aminopropyl triethoxysilane) was more proper because PVC was a kind of semipolar material.

Impact tests of PP composites with and without plerospheres were conducted according to GB/T 1043-1993 (a national standard of the People's Repub-

lic of China) with a Zwick pendulum impact tester (Germany) operated from −20 to 20°C. The impact specimens were 55 mm long, 6.5 mm wide, and 4.3 mm thick and had a small notch. After fracturing, the surfaces were studied with scanning electron microscopy (SEM), and the fracture surfaces of the specimens were coated with carbon. Tensile and flexural tests of PP composites with and without plerospheres were conducted at 23°C according to GB/T 1040-1992 and GB 1042-79 (national standards of the People's Republic of China), respectively, with an Instron universal testing machine (Shimadzu Co., Japan) operated at a 10 mm/min crosshead speed. Tensile specimens were made into dumbbell samples, and flexural specimens were made into rectangular strips 55 mm long, 10 mm wide, and 4.2 mm thick. Differential scanning calorimetry (DSC) measurements of PP composites with and without plerospheres were carried out with DSC-SP equipment from Rheometric Scientific, Ltd. (USA), at a heating rate of 10°C/min. Rheological tests of the UPVC composites with and without plerospheres were conducted on a Brabender plasticorder (Germany). The test temperature was 165°C, and the test rate was 5 rpm.

RESULTS AND DISCUSSION

Mechanical properties of plerosphere/PP composites

Impact properties

Figure 1 shows the notched impact strength of PP composites with various additions of modified plerospheres (0–30 wt %). The content of the coupling agent (silane) was 1%. The particle sizes of the fillers were 2 and 5 μm, and the test temperatures were −20 and 20°C.

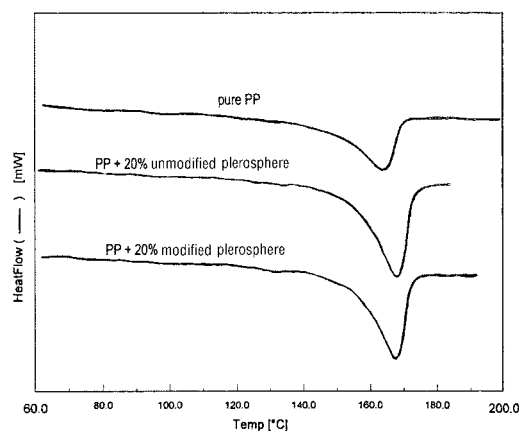As Figure 1 shows, the notched impact strength of PP composites increased with the addition of plero-

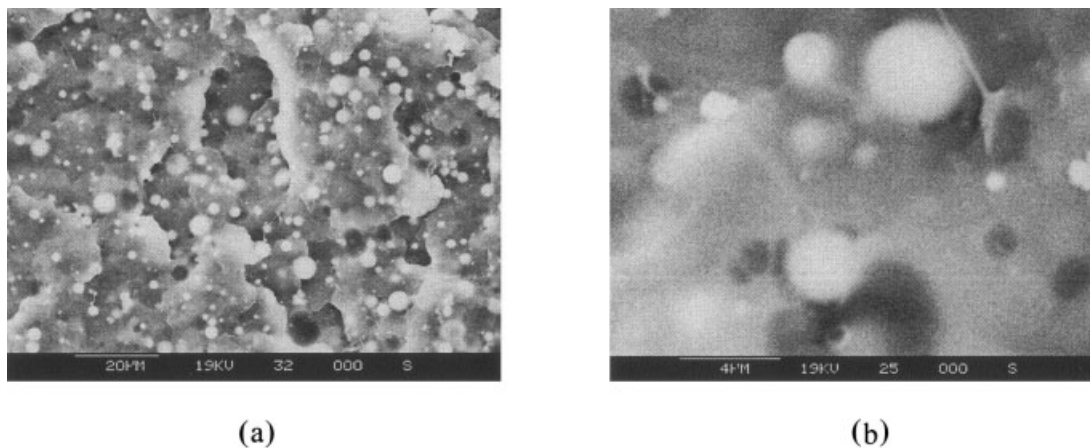**Figure 6** DSC endothermic thermograms of plerosphere/PP composites.

Figure 7 Impact fractographs of PP composites filled with 30 wt % plerosphere and 1% coupling agent: (a) 1000× and (b) 5000×.

spheres. At both −20 and 20°C, when the content of plerospheres was only 10 wt %, the notched impact strength improved greatly. At 20°C, as the filler content increased to 20 wt %, the notched impact strength further improved and reached a maximum value of 28% in the experiment. When the content of plerospheres increased to 30 wt %, the notched impact strength decreased to the value at which it was at 10 wt %. The changes in these properties meant that the mechanical properties of the composites did not increase linearly with increasing filler contents and that there was an optimum content for the best impact properties. However, when the particle size was 2 μm, the notched impact properties of the plerosphere/PP composites were better than those with a particle size of 5 μm. This meant that the finer the plerospheres were, the better the impact properties of the composites were.

Figure 2 shows the notched impact strength of PP composites with the filler modified and not modified by the coupling agent. At 20°C, the notched impact strength increased when the plerospheres were well modified with a coupling agent. The increase in the notched impact strength depended on the coupling agent, and the coupling agent I (A151) showed the better effect, whereas at −20°C, the notched impact strength changed little with the coupling agent.

Tensile and flexural properties

Figures 3 and 4 show the tensile and flexural properties of PP composites with various additions of modified plerospheres (0–30 wt %). The content of the coupling agent (silane) was 1%.

Figure 3 shows that the tensile properties of the PP composites improved with the addition of the filler. The tensile modulus increased quickly as the plerosphere content increased and was 80% higher than

that of the base polymer when the filler content was maximum in the experiment. Figure 4 shows that the flexural strength and flexural modulus also improved with increasing plerosphere contents.

Like the impact properties, the tensile and flexural properties of the plerosphere/PP material with a particle size of 2 μm were better than those of the material with a particle size of 5 μm. That is, the finer the filler was, the better the tensile and flexural properties of the composites were.

Figure 5 shows the tensile and flexural moduli of PP composites with modified and unmodified plerospheres. Figure 5 demonstrates that the tensile modulus increased with the addition of coupling agent I, but it decreased with the addition of coupling agent II. Figure 5 also shows that the flexural modulus increased with the addition of coupling agent I and coupling agent II, although coupling agent II showed a better effect.

Thermal properties

Figure 6 shows typical DSC endothermic thermograms of pure PP, PP composites with 20 wt % un-
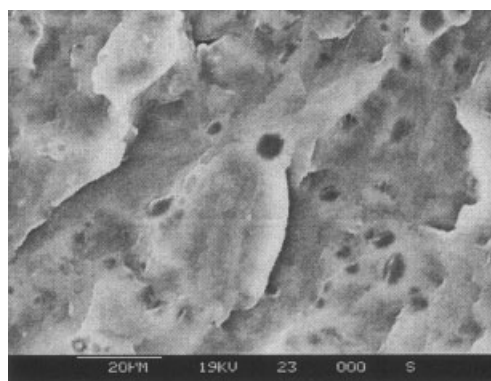

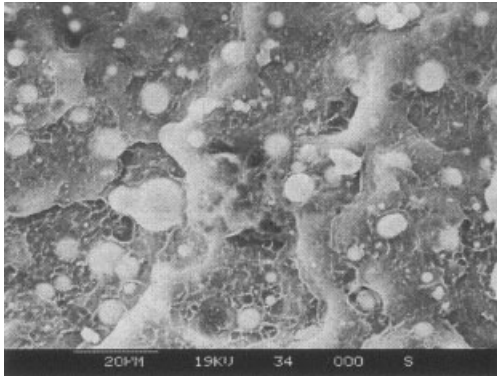**Figure 8** Impact fractograph of pure PP materials (1000×).

Figure 9 Impact fractograph of PP composites filled with 30 wt % plerosphere without the coupling agent (1000×).

modified plerospheres, and PP composites with 20 wt % modified plerospheres. The test temperature ranged from 60 to 200°C, and the heating rate was 10°C/min. In Figure 6, the DSC thermogram of pure PP shows that the endothermic peak was 164.3°C and that the heat of fusion was 96.3 J/g. The endothermic peak of the PP composites increased by 3–4°C and the heat of fusion decreased by 13–20 J/g with the addition of plerospheres. The endothermic peak of PP composites with the 20 wt % unmodified filler was 167.7°C, and the heat of fusion was 75.7 J/g. This indicated that the thermal properties of the PP material were improved and that the degree of crystallinity decreased with the plerospheres. However, the endothermic peak of the PP composite with the 20 wt % modified filler was 167.4°C, and the heat of fusion was 83.2 J/g; this

showed that the endothermic peak was independent of the coupling agent, whereas the heat of fusion increased with the addition of the coupling agent.

Figure 6 also shows that the endothermic peaks of pure PP and plerosphere/PP composites ranged from 164 to 168°C, and this indicated that PP, both in the pure state and in the composites, exhibited only the crystal form α because the melting temperature of α crystals is 160–176°C.[12]

SEM observations

The impact fracture surfaces of plerosphere/PP composites at room temperature were studied with SEM after the fracture surfaces were coated with carbon.

Figure 7(a,b) shows the impact fractographs of PP filled with 30 wt % modified plerospheres at different magnifications. The filler particles were dispersed well in the matrix, and the spherical particles of the plerospheres were well wetted with PP material. There was no clear separation or void at the interface of the composite. Figures 8 and 9 show SEM micrographs of the fracture surfaces of impact samples of pure PP and PP with 30 wt % unmodified plerospheres, respectively. In contrast, when the coupling agent was present, the adhesion between the filler and matrix was much stronger. Figure 7 also shows that there were some pores at the interface, but there were many more pores in the pure PP material (Fig. 8). These pores were produced during preparation because of the high shrinkage of PP.
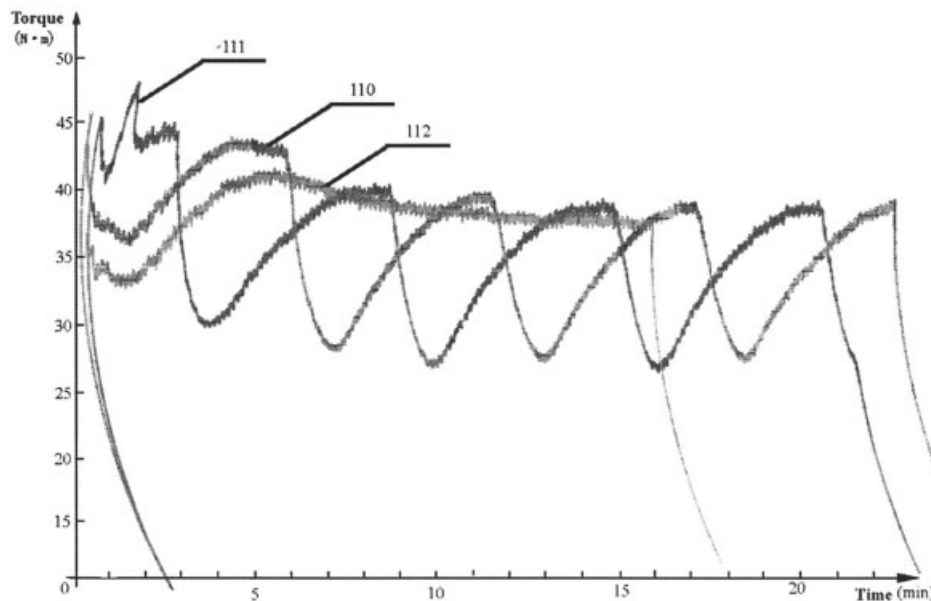

Figure 10 Torque versus time for PVC pipes filled with plerospheres.

TABLE I
Rheological Performance of the Plerosphere/PVC Composites Described in Figure 10

Specimen	Maximum torque (N m)	Relevant time (min)	Balanced torque (N m)	Relevant time (min)
110	46	0	Could not reach a stable gelation state	
111	48	0.5	Could not reach a stable gelation state	
112	41	4.5	38	13

Rheological behavior of plerosphere/PVC composites

The melt rheology of plerosphere/PVC composites was tested with a Brabender plasticorder. The particle size of the plerospheres was 2 μm. The temperature was 165°C, and the test rate was 5 rpm. The measurement range of the torque was 10–60 N m. Figure 10 shows the torque curve over time for the PVC pipes material with and without plerospheres, and Table I lists the relevant parameters for the rheological performance of the plerosphere/PVC composites described in Figure 10.

Figure 10 shows that the rheological behavior of a raw PVC pipe material (110) was very bad, and the maximum torque was 46 N m in the beginning. Even when the test time was 22 min, the system still did not reach a stable gelation state. For the PVC material with the addition of unmodified plerospheres (111), the maximum torque (48 N m) appeared when the time was 0.5 min. When the test time was 20 min, the system also did not reach a stable gelation state. However, for the PVC material with the addition of modified plerospheres (112), the maximum torque was only 41 N m when the time was 4.5 min, and when the test time was 13 min, the system reached a stable gelation state. The balanced torque was 38 N m.

These results indicated that the rheological behavior of the PVC pipe material was better in the presence of the plerospheres and coupling agent; the viscosity of the composites decreased, and the processability of the plerosphere/PVC pipe composites improved. Most importantly, the composites reached a stable gelation state quickly, and the maximum torque decreased. Furthermore, the rheological performance of the plerosphere/PVC composite without the coupling agent was even worse, in that the compatibility between the plerospheres and PVC matrix was poor when the coupling agent was absent. This suggested that the coupling agent was very important for the plerosphere/PVC pipe composites.

CONCLUSIONS

Plerospheres were used as fillers for PP and PVC materials. With a filler content of 0–30 wt %, the impact strength of PP composites increased and further increased when the plerospheres were modified with 1 wt % silane A151. The tensile and flexural properties increased with the addition of plerospheres and further increased with increasing filler content. When the filler content was 30 wt %, the tensile and flexural properties were best. Moreover, the mechanical properties were enhanced when the particle size decreased. When PP was filled with plerospheres, the shrinkage of PP material decreased, and the thermal properties of PP composites improved. For PVC pipe material, the rheological behavior improved greatly when the material was filled with modified plerospheres, which could be very important to practical production.

Generally, the toughness of a filled polymer composite decreases when the strength increases. However, in this study, both the strength and toughness of plerosphere/PP composites increased.

This study shows the beneficial use of a coal combustion byproduct. Plerospheres, a new multifunctional material, may bring great social and economic benefits and, at the same time, prevent environmental pollution.

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