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Synthesis of polypropylene composites with modified calcium sulfate whisker prepared from shale vanadium neutralization slag

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ABSTRACT

In this study, the solid waste of shale vanadium neutralization slag (NS) was effectively utilized by preparing calcium sulfate whisker (CSW) filler and reinforcing polypropylene (PP) matrix. The stabilization and modification mechanism of stearic acid on CSW were analyzed. The results showed that stearic acid blocked the hydrophilic active sites of CSW by chemical links with the whisker surface to inhibit whisker hydration and organically modify the whisker with an active index of 0.72. NS/PP, modified NS(MNS)/PP and MCSW/PP composites were synthesized via melt extrusion and injection molding. The effects of whiskerizing and modification of NS on the mechanical properties and thermal properties of the composites were evaluated. The results showed that MCSW improved the thermal stability of PP with a 51 °C increase at 10 wt% filler content. PP matrix filled by MCSW has better elasticity and stickiness than MNS. Modified fillers have better dispersion and compatibility with PP matrix than unmodified NS particle. MCSW fractured or pulled out to uniformly transfer stress, indicating strong interfacial adhesion between CSW and matrix. MCSW has stronger heterogeneous nucleation than MNS to induce the transformation of α-crystalline form to β-crystalline form, which resulted in better performance in mechanical and thermal properties.

Introduction

In the typical process of acid leaching vanadium from vanadium-bearing shale, the acid leaching solution is obtained from vanadium-bearing shale after crushing, roasting and acid leaching process, pH of which is generally less than 0.5. In order to meet the requirements of subsequent extraction with optimal pH of 2.0–2.5, the acid leaching solution is usually needed to be neutralized by lime, thereby producing a large amount of shale vanadium neutralization slag (NS) [1]. NS is white or light yellow solid, fine granularity, and the main component is calcium sulfate hemihydrate or anhydrous calcium sulfate, which belongs to typical gypsum base solid waste. Random accumulation of the NS will cause the land occupation and environment pollution, due to absorption and entertainment of trace amounts of heavy metal impurities (V, Zn, Cr, etc). Taking full account of these chemical and physical properties, An effective way to utilize NS is to prepare high-performance calcium sulfate whisker (CSW) inorganic filler. Generally, CSW is prepared from natural gypsum [2] or phosphogypsum [3], desulfurization gypsum [4] and other industrial solid waste [5]. Its perfect structure, specific cross sectional area and stable size give it high modulus, high temperature resistance, excellent mechanical properties and many other advantages, so that it is widely used as the functional filler in plastics industry [6].

However, the surface of hemihydrate calcium sulfate whiskers (CSH) from hydrothermal synthesis of NS exist a large number of hydrophilic active sites (Ca^{2+}, OH^{-}, etc), which made itself in a thermodynamics unstable state and very easy to be hydrated to dihydrate calcium sulfate whisker (CSD) with poor morphology and property [7]. As a result, the use of such calcareous waste had been limited. Yang et al. [8] stabilized CSH by calcining at 700 °C for 4 h, obtaining stable morphology but high production cost. Yuan et al. [9] used sodium oleate as stabilizer to prevent whisker hydration by closing whisker surface hydrophilic active sites, but the stable time is limited and whisker growth is easy to be affected. Meanwhile, CSW needs to be organically modified before filling in plastics for poor compatibility and dispersion with the polymer matrix. The modification mechanism is usually that the modifier adsorb on the surface of powder by the bonding of the hydrophilic side with the powder, and the hydrophobic side of the modifier makes the powder present hydrophobicity [10,11]. Stearic acid was chosen to stabilize and modify CSW in this study,

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which can not only achieve stable crystal morphology but also make the surface organic.

PP is one of the most widely used general-purpose plastics, some researchers have investigated the application of CSW in PP. Radhakrishnan and Saujanya [12,13] studied PP/$CaSO_4$ composites and found that CSW improved tensile modulus and impact strength of the composites for heterogenous nucleation. Wang [14] found the notched Izod impact strength of PP was dramatically increased by adding CSW along with the Titanate coupling agent NDZ-401. The dispersion of CSW and the interfacial bond between CSW and matrix were the main elements to influence the mechanical properties of the composites, and the load transferring might be the reinforcement mechanism. Qin et al. [15] found that ultrasound treated CSW could improve the β-nucleation capacity of PP and resulted in increased β-crystal form to toughen the composites. However, all of the raw material of these investigations were pure CSW products. Few of them paid attention to the source of the whisker, not to mention its stability. The practical value of application needed to be studied in depth. Except for this, the different effects of particles and whiskers on polymers are rarely reported, so this study not only solved the problem of the preparation of CSW, but also discussed the enhancement of whisker on PP.

In this study, stable CSW filler was firstly prepared from NS by hydrothermal synthesis and modification treatment. Stability mechanism of the modifier was simply analyzed. Then, NS/PP, MNS/PP and MCSW/PP composites containing different filler contents were prepared by melt extrusion and injection molding. The effects of modification and whiskerizing of NS on the mechanical properties, interfacial morphology, crystallization and thermal properties of the composites had been investigated.

Experimental

Materials

The NS used in this study is laboratory self-made income according to vanadium-bearing shale acid leaching process [16]. The chemical composition of the NS was analyzed by ICP-AES. Table 1 shows that CaO(33.00%), SO_3(45.92%) are the major compounds with very few P_2O_5(1.29%), Fe_2O_3(1.01%), Al_2O_3(1.49%) impurities. Particle size analysis of the NS was carried out by the means of laser particle size distribution instrument. It can be found in Table 2 that the particle size of more than 90% NS was below 40 μm, which is reasonably fine for filler. The XRD pattern of the NS (Fig. 1) shows that the main component are CSH and a few calcium sulfate, which is similar to natural gypsum. The SEM image (Fig. 2) shows that the micromorphology is fine grainy or flaky. All above indicate that the NS is suitable raw material for preparation of CSW.

Stearic acid (analytically pure) was purchased from National drug group chemical reagents Co., Ltd. (Shanghai, China). PP(T30S) was purchased from Xuzhou Kuanghui Plastic Co., Ltd. (Xuzhou, China). $MgCl_2{\cdot}6H_2O$ (analytically pure) was purchased from National drug group chemical reagents Co., Ltd. (Shanghai, China).

Preparation of MCSW

MCSW was prepared as follows: 30 g of the NS and 970 ml of distilled water were added into a 2 L autoclave (GSH-2, Weihai Chaoyang Chemical Machinery Co., Ltd. China). In the meantime, 3 g of $MgCl_2{\cdot}6H_2O$ was added into the slurry. The slurry was then heated at a constant temperature of 130 °C for 6 h and stirred at a constant rate of 200 rpm. After reaction, the autoclave was cooled to 100 °C, and the suspension was rapidly filtered. The filter cake was directly added into a 500 ml three-necked round-bottom flask with 380 ml hot anhydrous ethanol solution dissolved 1 g stearic acid. The mixture was stirred at 90 °C water bath for 20 min. The mixture was then hot filtered and dried at 105 °C for 2 h and the stable MCSW was prepared.

Table 2
Particle size distribution of NS.

Grain size	+ 40 μm	40–30 μm	30–20 μm	20–10 μm	− 10 μm
Content, wt%	9.97	11.36	13.33	21.44	43.90

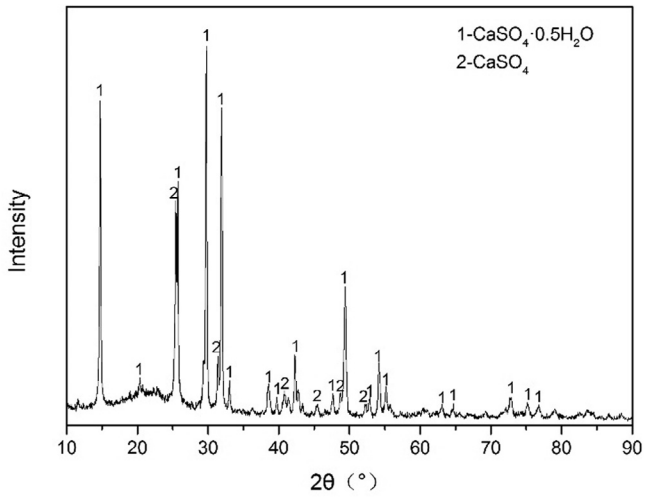

Fig. 1. XRD pattern of NS.

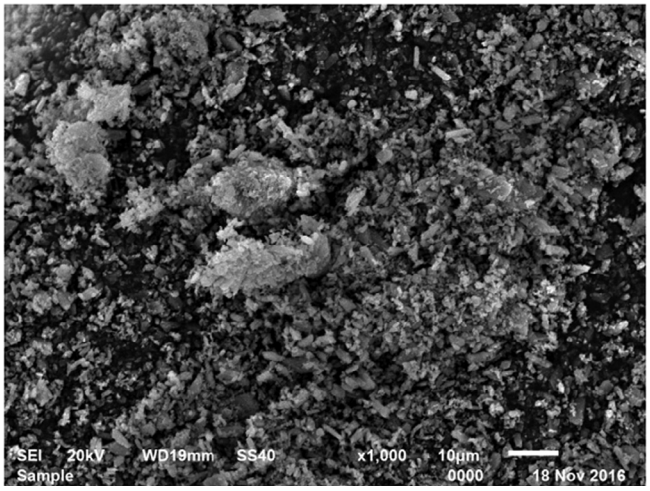

Fig. 2. SEM image of NS.

Preparation of PP composites

PP composites were prepared as follows: PP and NS, MNS, MCSW with different filling contents (0, 5, 10, 15, 20, and 25 wt%) were mixed

Table 1
Main chemical composition of NS.

Element	CaO	SO_3	P_2O_5	Fe_2O_3	SiO_2	Al_2O_3	TiO_2	V_2O_5	Loss
Content, wt%	33.00	45.92	1.29	1.01	0.28	1.49	0.49	0.07	16.45