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RESEARCH ARTICLE

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Effect of unsaturated hydroxyl-fatty acid modified nano-CaCO$_3$ on the morphological and rheological behavior of PP

Abstract A modified nano-calcium carbonate (R-CCR) was prepared by coating a layer of unsaturated hydroxyl-fatty acid on the surface of CCR powders using a solid state method; the latter were commercial nano-CaCO$_3$ modified with stearic acid. FTIR studies indicate that the modifier is combined on the surface of CaCO$_3$. PP/EPDM/nano-CaCO$_3$ ternary composites were prepared by a melt-mixing method. SEM and TEM were utilized to examine the morphology of the composites. The tensile fractured surface of PP/EPDM/R-CCR showed a fibroid morphology and large-scale yield deformation. The impact fractured surface showed that the amount of cavities in the PP/EPDM/R-CCR system was increased, however their size diminished obviously. R-CCR particles were dispersed uniformly in the PP matrix, and their compatibility was distinctly improved as compared to CCR when the amount of R-CCR was 15 h^{-1}. The tensile strength remained nearly constant (reduced from 27.6 MPa to 27.5 MPa), while the impact strength increased from 9.6 kJ/m^2 to 15.4 kJ/m^2 as CCR was replaced by R-CCR. Meanwhile, the bending strength and bending modulus also increased correspondingly. Furthermore, the impact strength of PP/EPDM/R-CCR was maintained at a high level (15.4 kJ/m^2), which was more than the sum of that of PP/EPDM and PP/R-CCR (6.6 kJ/m^2 and 6.1 kJ/m^2 respectively). This indicates that the R-CCR and EPDM have a significant synergistic toughening effect on PP while maintaining the strength and modulus of virgin PP. Both the storage modulus G' and loss modulus G'' of PP/EPDM and PP/EPDM/R-CCR composites increase with increasing frequency, but the values of G' and G'' of the tertiary composite are relatively higher than those of the binary system. The loss factor and viscosity decrease with increasing frequency, but there is little difference between tertiary and binary composites. The apparent viscosity η of the tertiary system containing R-CCR is lower than that of the tertiary system containing CCR and virgin PP. The viscosity of the composites sig-nificantly decreases with increasing shear rate. The mea-sured mechanical properties of the composites indicate that replacing CCR with R-CCR for binary composites could simultaneously enhance the toughness and strength of PP.

Keywords modified nano-CaCO$_3$, polypropylene, morphology, rheological behavior, mechanical properties

The mechanical properties of materials are closely correlated to their morphological and rheological behavior. One of the foremost characteristics of polymers is that their macroscopic performance can be controlled by changing their microstructure at a nanometer scale. The relation of the structure and performance of polymers could be analyzed by studying the morphological and rheological behavior of different filled composites. The results have primary meaning in determining the conditions for preparation and processing of composites.

The rheological behavior of composites is an important means to evaluate the dispersion of nanoparticles in a polymer matrix because the rheological behavior of composites is sensitive to the shape, size, dispersion and content of nanoparticles. Thus, the relation between the microstructure and rheological behavior of composites can be built up based on rheological tests, and the results will be beneficial to the processing of composites.

Fillers can improve the mechanical properties of materials, but their fluidity and processing behavior may become worse at the same time. Solomon [1] studied the linear and non-linear rheological behavior of PP/MMT (MMT: montmorillonite) composites using a torsion rheometer at low shear rates. The results showed that the layer space of MMT was extended, and a short-range order remained unchanged during the melt intercalation. Krishnamoorti [2] investigated the rheological behavior of poly (dimethyldiphenyl siloxane)/MMT intercalated hybrids

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with MMT contents of 8 wt% and 15 wt%. The steady-shear rheological behavior showed that the pure polymer exhibited Newtonian behavior at low shear rates and shear thinning at high shear rates. The intercalated nanocomposites showed an increase in viscosity at all shear rates and exhibited shear thinning at all shear rates. With increasing shear rate the polymer and the exfoliated hybrids exhibited shear thinning, and with the shear-thinning, character setting occurred at lower shear rates with increasing silicate content, increasing monotonically with increasing silicate loading (at a fixed-shear rate). It is believed that the shear thinning behavior was a result of the end-tethering of the polymers to the layered silicate, which arranged themselves as randomly oriented grains (wherein some local order was maintained) with the presence of intergranular defects. Unusual rheological behavior of polyolefin/nano $CaCO_3$ composites was studied by Chen [3]. For the first time, it was found that within a wide range of $CaCO_3$ content and under good dispersion conditions, the larger the proportion of nano $CaCO_3$, the lower the composite apparent viscosity and the better the fluidity. By proper surface treatment, the critical shear rate/stress of the composites was enhanced remarkably, and the processibility was improved. Zhang [4] studied the rheological behavior of PP/POE/nano-$CaCO_3$ composites. With increasing nano-$CaCO_3$ content, the apparent viscosity of the melt increased at low shear rates and decreased at higher shear rates. The viscosity increased with increasing POE content. The composite melt exhibited a non-Newtonian behavior of shear thinning, and the non-Newtonian index decreased with the addition of nano-$CaCO_3$.

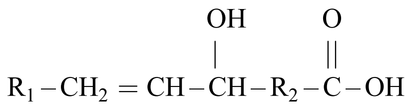
Elastomers and nanometer scale inorganic particles are two important modifiers for polyolefines. Elastomer modification could improve the toughness of polyolefines, however, the preparation cost is increased, and the heat stability, rigidity and strength are decreased [5–7]. Nanometer scale inorganic granules not only may reduce the cost [8–11], but also overcome the disadvantages of elastomer modification. An approach with mild mixing conditions has been demonstrated for the preparation of polymer/$CaCO_3$ nanoparticle composites in a twin-screw extruder by Liu [12]. In this method, the pre-dispersed nanoparticle suspensions were blended with melting polymers, PP, PE, PC and PBT in a weak shearing field using an extruder, followed by removing the water from the vent. The dispersion quality of nano-$CaCO_3$ in the matrix of these polymers was characterized by scanning electron microscopy (SEM), and the nano-$CaCO_3$ was found to be dispersed in a polymer matrix at the nanoscale. The data on the molecular weight of PC and its nanocomposites showed that degradation did not occur in the process. The mechanical properties of composites had increased slightly, with a content of 1.5 wt% nano-$CaCO_3$. This proved that the approach was suitable for the preparation of composites with polar and non-polar polymers. Tan [13] investigated the crystal morphology, internal structure of the dispersed phase, and the phase morphology for two impact polypropylene copolymers (IPC) with the same ethylene content, rubber content, relative molecular weight and relative molecular weight distribution, but with obviously different toughness, using polarized optical microscopy, differential scanning calorimetry, wide angle X-ray diffraction, dynamic mechanical analysis and atomic force microscopy. It was found that the crystallization morphology and behavior of both samples were similar, but the compatibility between the dispersed phase and the matrix in IPC-A was better than that in IPC-B. Moreover, phase composition of the matrix and the dispersed phase of the different IPCs were analyzed. It was found that the dispersed phase displayed a complex concealment structure. Models of phase structure were proposed to describe the phase structure of both IPC heterophase systems, and the action of E-b-P in the IPC. It was suggested that phase morphology played a more important role as a compatibilizer in enhancing the impact strength of IPC.

In this paper, the rheological behavior of PP and its composites are investigated by torsion rheometry. Within a certain range and under constant shear rates, the increase in melt viscosity may reduce the fluidity and processibility of polymers, whereas decreasing the melt viscidity, fluidity and the processibility can be improved. Therefore, the effect of the modified nano-$CaCO_3$ on PP melt viscosity and processibility is characterized by the relation of viscosity versus shear rate. The morphology of composites is analyzed at the same time.

1 Experimental

1.1 Materials

PP (F401) is a commercial product produced by Lanzhou Petrochemistry Ltd, China. CCR is a commercial nano-$CaCO_3$ modified with stearic acid, Guangping Chemical Ltd, Guangdong, China. Ethylene-propylene-diene mischpolymer (EPDM 4045) is a commercial product supplied by Mitsui Ltd, Japan. The modifier, an unsaturated hydroxyl-fatty acid, is a refined product produced by Panyu Nanxin Chemical Ltd, Guangdong, China. There are unsaturated double bonds, hydroxides and carboxyls in its molecular structure, as follows



$$R_1-CH_2=CH-\overset{OH}{\overset{|}{CH}}-R_2-\overset{O}{\overset{||}{C}}-OH$$

where R_1 and R_2 represent different alkyls.

1.2 Preparation and characterization of modified nano-$CaCO_3$

R-CCR was prepared by high speed mixing of CCR and 3% unsaturated hydroxyl-fatty acid in a blender at 80°C for 15 min.

A Nicolet MEGNA-IR 760 Fourier transform infrared spectrometer (FTIR) was used to identify the CCR and R-CCR. Before scanning, the nano-$CaCO_3$ powders were extracted with $CHCl_3$ for 48 h and dried in a vacuum oven at 60°C to constant weight. The dried powders were mixed with KBr, and tablets were made for measurements; the wavenumber range was 4000–400 cm^{-1}.

1.3 Preparation and characterization of composites

PP/EPDM(100/10) and nano-$CaCO_3$ composites were obtained by mixing the components in a twin-roll mill at 160–180°C, then 4 mm thick sheets of these compounds were prepared by compression molding (180°C, 10 Mpa, 5 min). The samples were cut into standard shapes and sizes for the testing of mechanical properties after 24 h.

A LEO-1530VP Philip XL30 scanning electron microscope (SEM) was utilized to observe the morphology of PP/EPDM/nano-$CaCO_3$composites. Before electron microscopy observation, the composites were coated with Au using a SEM Coating Unit (RMC-eiko Co., Japan).

A Rheometric Science RDA III rheometer was conducted to test the storage modulus G′(Pa), loss modulus G'' (Pa) and viscosity η^* (Pa·s). The diameter of the parallel plate disk was 2.5 mm, the gap was 1.0 mm, and the frequency range was 0.1–500 rad/s.

The tensile strength of samples was tested at an electronic tensile tester (Shimadzu AG-1, 10 kN, Japan), according to GB/T1040–92. The bending strength and modulus were tested at an electronic tester (Instron5500, USA), according to GB9341–88. The impact strength was tested at an impact tester (Zwick 5113.300, Germany), according to GB/T1843–1996.

2 Results and discussion

2.1 FTIR spectral analysis of R-CCR and CCR

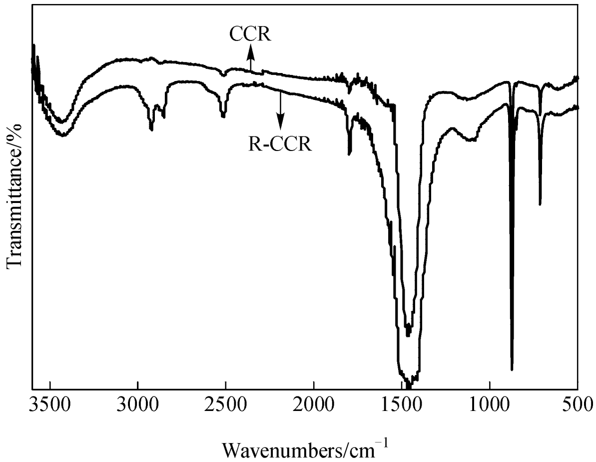


Fig. 1 FTIR spectra of R-CCR and CCR

Figure 1 shows the FTIR spectra of extracted R-CCR and CCR. The C–O stretching absorption band at 1458 cm^{-1} for CCR was widened with a shift of 7 cm^{-1} to high wavenumbers for R-CCR. In the spectrum of R-CCR, two new peaks at 2924.6 and 2856.1 cm^{-1} for the $–CH_2$ and $–CH_3$ stretching absorption bands appeared. The appearance of these bands for R-CCR indicated that the modifier grafted onto the surface of nano-$CaCO_3$. There were no–CH_2 and $–CH_3$ stretching absorption bands in the spectrum of CCR. This showed that stearic acid was only physically coated onto the surface of nano-$CaCO_3$ and was extracted right away by $CHCl_3$.

2.2 SEM analysis of composites

Figure 2 shows the SEM photographs of impact fracture surfaces of PP/EPDM/CCR and PP/EPDM/R-CCR composites. Figure 2(a) shows the SEM photograph of PP/EPDM(100/10). It shows the slippery surface and the character of a slight tough fracture. It indicates that PP filled with rubber is propitious for the change from brittleness fracture to toughness fracture.

Figure 2(b), (c) shows the SEM photographs of PP/EPDM/CCR(100/10/15) with different magnifications. They show the slippery surface and the character of a slight tough fracture. The CCR particles agglomerate together and have a clear interface. This indicates that the binding force of CCR particles to the PP matrix is weak. The particles are easily pulled out from the matrix under impact, and the composites have weak toughness. Figure 2(d), (e) shows the SEM photographs of PP/EPDM/R-CCR(100/10/15) with different magnifications. They show a rough surface with a beehive structure and the typical morphology of a yield fracture. R-CCR particles disperse uniformly and finely in the PP matrix, and there are many fine cavities around the R-CCR particles. All these indicate an improved interfacial compatibility between R-CCR and polymer matrix.

Figure 2(f), (g) shows the SEM photographs of PP/EPDM/R-CCR(100/10/20) with different magnifications. They show rough surfaces and toughness fractures. The particles disperse poorly and agglomerate together. The defective interface is formed by the filler agglomeration and reduces the roughness of the materials. This is a match with their mechanical properties.

Figure 3 shows the SEM photographs of the impact tensile surface of PP/EPDM/CCR and PP/EPDM/R-CCR composites. The tensile fracture of PP/EPDM and PP/EPDM/CCR shows the morphology change from brittleness fracture to toughness fracture. However, the tensile fractured surface of PP/EPDM/R-CCR is rough and appears as a fibroid structure with large-scale yield deformation, indicating the typical morphology of a tough fracture. R-CCR and EPDM have a synergistic toughening effect on PP. This is conformable with its mechanical properties.

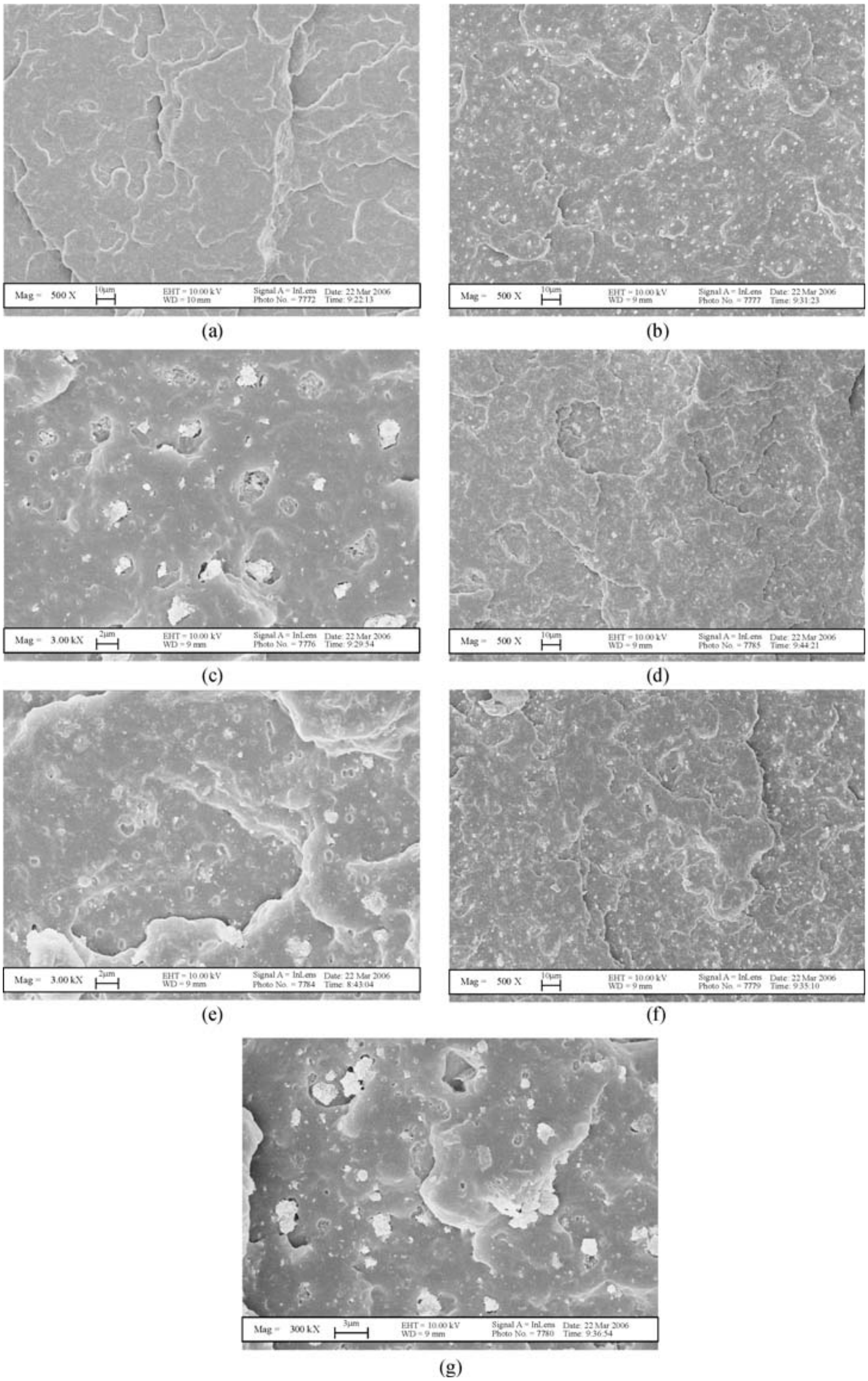
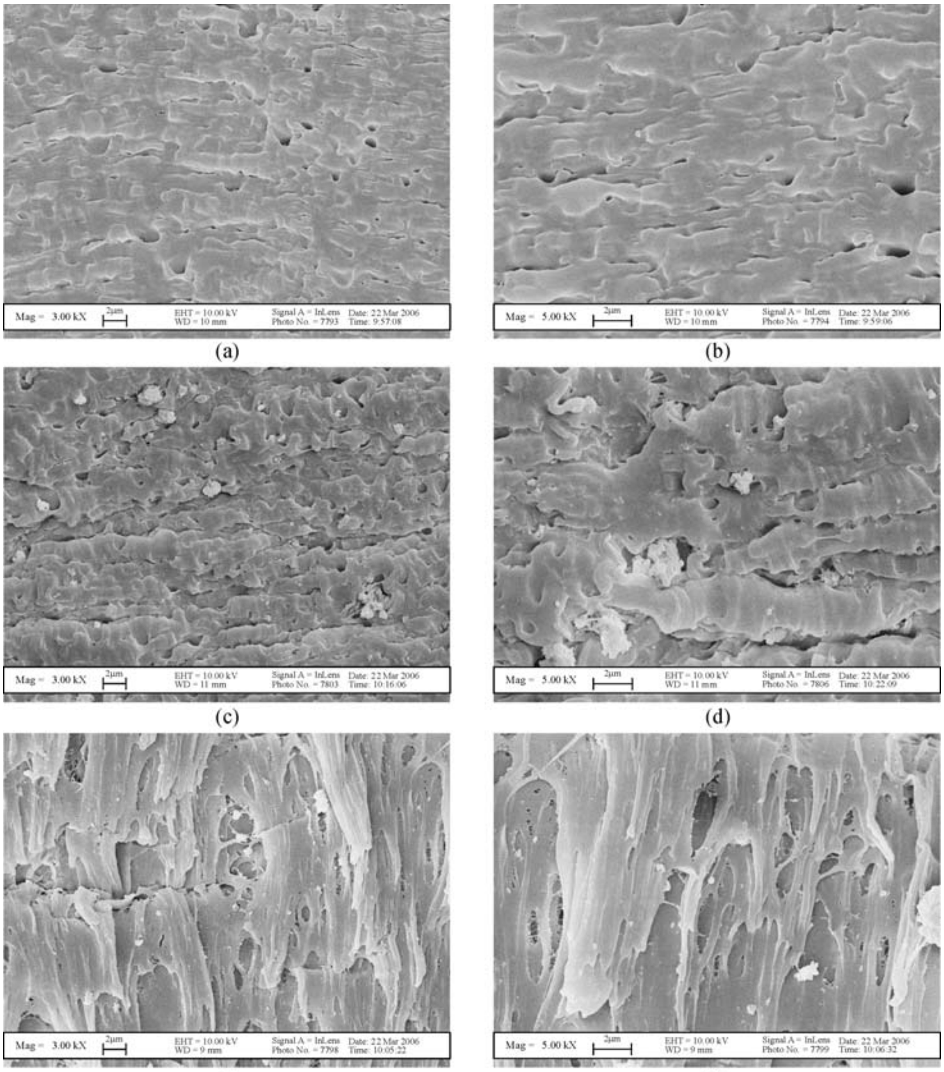


Fig. 2 SEM photographs of impact fracture surface of PP/EPDM and nano-$CaCO_3$ composites: (**a**) PP/EPDM (100/10); (**b**) PP/EPDM/CCR (100/10/15); (**c**) PP/EPDM/CCR (100/10/15); (**d**) PP/EPDM/R-CCR (100/10/15); (**e**) PP/EPDM/R-CCR (100/10/15); (**f**) PP/EPDM/R-CCR (100/10/20); (**g**) PP/EPDM/R-CCR (100/10/20)

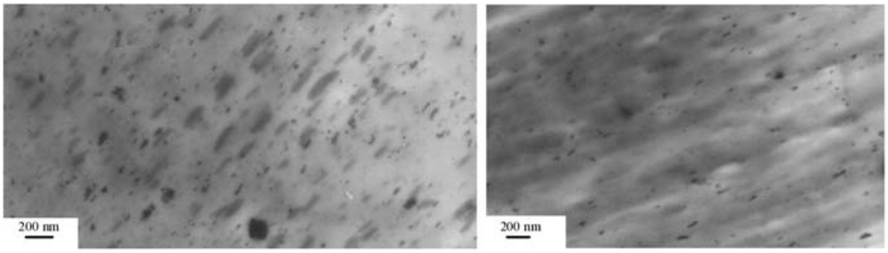
2.3 TEM analysis of composites

Figure 4 shows the TEM photographs of PP/EPDM/nano-$CaCO_3$(100/10/6) composites. They show that both CCR and R-CCR disperse at nanometer scale in the PP matrix. There is a sea-island structure with a clear interface in the system of PP/EPDM/CCR. On the other hand, no clear sea-island structure is found in the PP/EPDM/R-CCR system.



(a) (b) (c) (d) (e) (f)

Fig. 3 SEM photographs of tensile fracture surface of PP/EPDM and nano-$CaCO_3$ composites: (**a**) PP/EPDM (100/10); (**b**) PP/EPDM (100/10); (**c**) PP/EPDM/CCR (100/10/9); (**d**) PP/EPDM/CCR (100/10/9); (**e**) PP/EPDM/R-CCR (100/10/9); (**f**) PP/EPDM/R-CCR (100/10/9)



(a) (b)

Fig. 4 TEM photographs of PP/EPDM/CCR and PP/EPDM/R-CCR composites: (**a**) PP/EPDM/CCR(100/10/6); (**b**) PP/EPDM/R-CCR(100/10/6)

It indicates that the interfacial compatibility of PP and EPDM is improved by filling with R-CCR, and EPDM and R-CCR are uniformly distributed in the PP matrix. So the PP/EPDM/R-CCR composites have good comprehensive properties.

2.4 Rheological behavior of composites

Figure 5 gives the dynamic rheological curves of PP/EPDM/R-CCR composites. It shows that both the storage modulus G' and loss modulus G'' of PP/EPDM/R-CCR composites increase with increasing R-CCR content and are higher than those of the PP/EPDM system. The increase of G' is attributed to the high modulus of nano-CaCO$_3$. The increase of G'' is attributed to the coating of a soft polymer layer on the surface of nano-CaCO$_3$, which could entwine or react with EPDM and PP chains and improve the interface interaction. Thus, the energy dissipation of the composites under shear stress is increased, and the toughness of materials is improved. These results indicate that the rigidity and roughness of PP/EPDM composites were improved at the same time by adding R-CCR.

The viscosity of composites increases with increasing filler content. However, a viscosity decrease was observed at low filler content (6h^{-1}). This indicated that nano-CaCO$_3$ could be a lubricant filler at low content. The loss factor (tanδ) increase showed that the move-ment of PP chains in composites was more affected by shear stress as compared to that in pure PP. This is cau-sed by the restriction of movement of PP chains in composites.

The effect of R-CCR on the melt viscosity and processibility of composites could be evaluated by the relation of viscosity versus shear rate. Figure 6 shows the viscosity versus shear rate of the PP/EPDM/CCR (100/10/3) and PP/EPDM/R-CCR(100/10/3) composites. The composites show a decrease in viscosity with increasing shear rates, exhibiting the characteristics of pseudo-plastic fluids. The viscosity decrease with nano-CaCO$_3$ loading indicated that the processing of the PP/

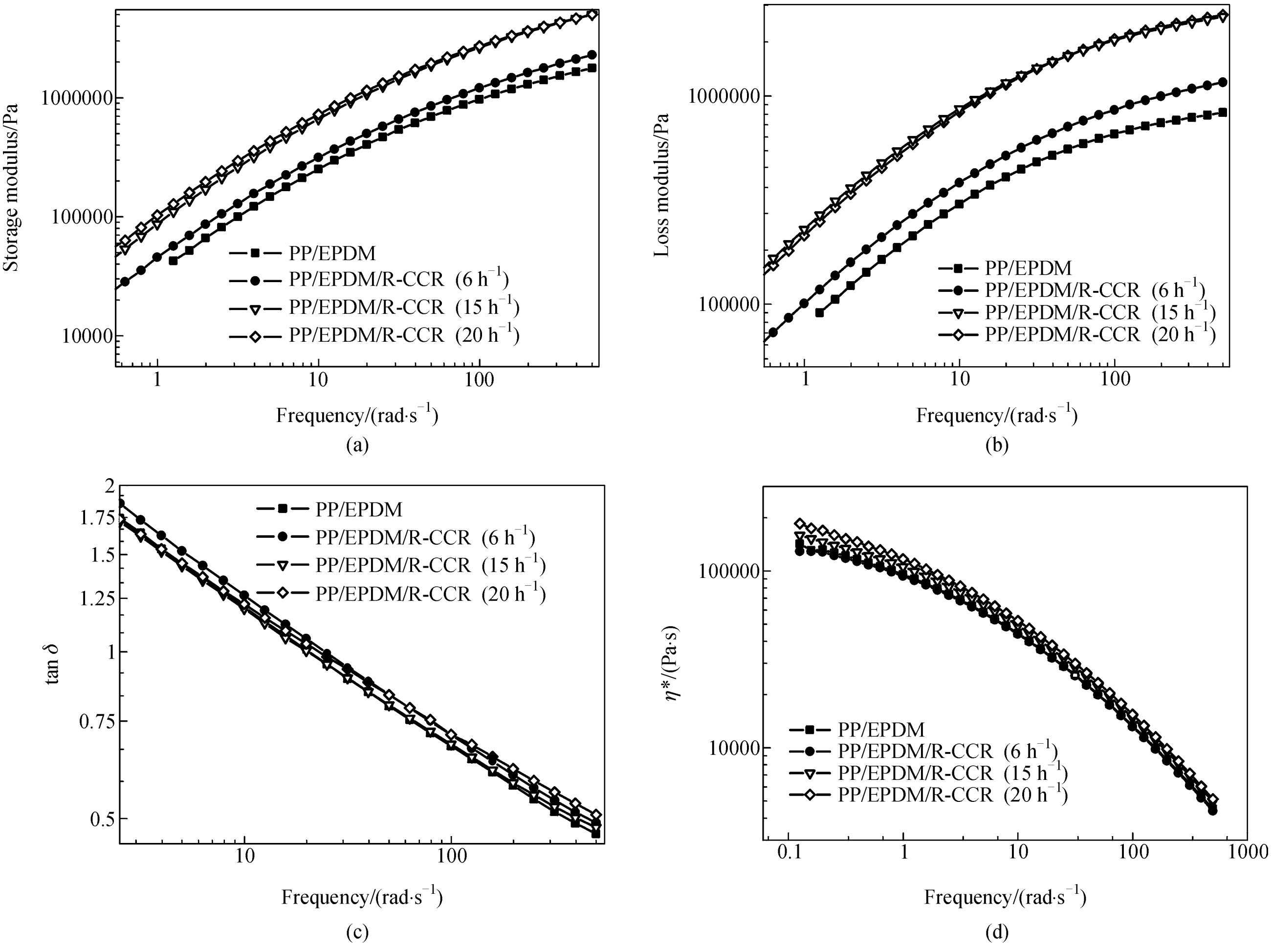


Fig. 5 Dynamic rheological curves of PP/EPDM/R-CCR composites: (**a**) G' versus frequency; (**b**) G'' versus frequency; (**c**) tanδ versus frequency; (**d**) η^* versus frequency

Table 1 Mechanical properties of PP/EPDM filled with different nano-$CaCO_3$

Sample	Tensile strength /MPa	Impact strength /($kJ \cdot m^{-2}$)	Bending strength /MPa	Bending modulus /MPa
PP	36	4.8	58	1760
PP/CCR(100/6)	35.3	5.2	60	1950
PP/R-CCR(100/6)	38.2	6.1	68	2130
PP/EPDM(100/10)	30.3	6.6	42.0	1202
PP/EPDM/CCR(100/10/15)	27.6	9.6	46.6	1648
PP/EPDM/R-CCR(100/10/15)	27.5	15.4	47.3	1720

EPDM system could be improved by nano-$CaCO_3$ loading. The viscosity de-crease of the PP/EPDM/R-CCR system is greater than that of the PP/EPDM/CCR system. This shows that R-CCR is superior to CCR in improving the processing of PP/EPDM blends.

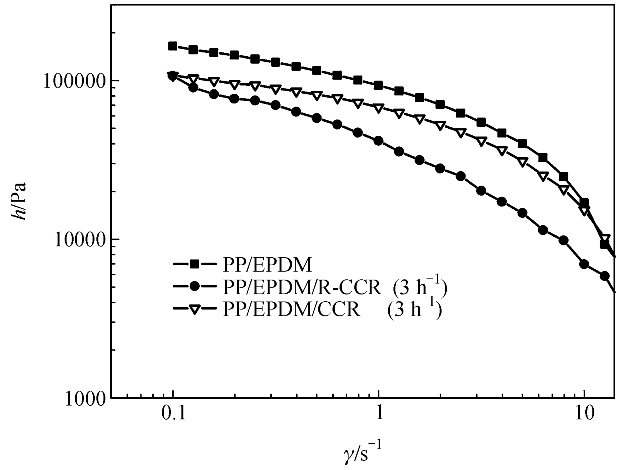


Fig. 6 Viscosity versus shear rate of PP/EPDM/CCR and PP/EPDM/R-CCR composites

2.5 Mechanical properties

The mechanical properties of PP/EPDM/nano-$CaCO_3$ composites with 100/10 of PP/EPDM and various amounts of nano-$CaCO_3$ are listed in Table 1. As compared with PP/EPDM, the enhancement of impact strength, bending strength and bending modulus of PP/EPDM/R-CCR is obvious, while the tensile strength only loses a few percent. The mechanical properties of PP/EPDM/R-CCR composites are much better than those of the PP/EPDM/CCR composites. For example, in the case of an R-CCR content of 15 phr, the impact strength increases by 61% from 9.6 to 15.4 kJ/m^2, the bending stre-ngth and bending modulus also increase correspondingly, while the tensile strength only decreases by 0.36% from 27.6 to 27.5 MPa. The impact strength of PP/EPDM/R-CCR (15.4 kJ/m^2) is higher than the sum of that of PP/EPDM (6.6 kJ/m^2) and PP/R-CCR(6.1 kJ/m^2). This suggests that R-CCR and EPDM have a synergistic toughening effect on PP.

In summary, unsaturated hydroxyl-fatty acid modified nano-$CaCO_3$ (R-CCR) and EPDM exhibited an obvious toughening effect on PP. The tensile and impact fractured surfaces of PP/EPDM/R-CCR showed the typical morphology of a tough fracture and large-scale yield deformation. R-CCR dispersed uniformly in the matrix and had good interfacial compatibility. The toughening effect of R-CCR on PP was much better than that of the stearic acid-modified commercial nano-$CaCO_3$(CCR). The processibility of PP composites was not worsened by adding R-CCR.

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