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# Thermal stability, flame retardancy and rheological behavior of ABS filled with magnesium hydroxide sulfate hydrate whisker

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## Summary

Halogen-free and flame-retardant acrylonitrile–butadiene–styrene copolymer (ABS) composites were prepared using magnesium hydroxide sulfate hydrate (MHSH) whisker as a flame retardant, and the effect of zinc stearate ($ZnSt_2$) as a dispersion additive on the morphology and properties of the ABS/MHSH composites was studied. The morphology observation by using scanning electronic microscope (SEM) indicates that the addition of zinc stearate could improve the dispersion of the MHSH whisker in ABS matrix. Cone analysis results show that the heat release rate (HRR) and mass loss rate (MLR) of the composites decrease considerably with increasing MHSH whisker content. The composite with zinc stearate has lower HRR than the composite without zinc stearate, indicating the better dispersion of MHSH whisker could improve the flame retardancy of ABS composites. SEM observation results show that the char residue of ABS/MHSH composites retain its fibrous appearance. Thermogravimetric analysis (TGA) shows that the presence of MHSH enhanced thermal stability of the composites obviously. The viscoelastic behavior of the composites was measured by using a parallel plate rheometer. With increasing MHSH whisker content, the viscosity, storage modulus of the composites increase at low frequency zone, and ABS/MHSH composites exhibit more distinct solid-like response at terminal zone than ABS. The presence of zinc stearate leads to slight increases in the storage modulus.

## Introduction

ABS is a kind of widely used thermoplastic copolymer because it has many attractive properties such as good processability, chemical resistance and low cost. However, ABS also has several limitations, namely, low thermal stability, poor flame retardancy and poor chemical resistance. How to gain a balance between reinforcement and flame retardancy is a common problem facing material researchers and producers [1, 2].
As one-dimensional functional materials, whiskers have attracted great attention because they exhibit curious structure and various remarkable physical, chemical, and

mechanical properties which are distinctive from those of conventional bulk materials [3]. Because of their surface perfection and high elastic strength, whiskers will undoubtedly be of great interest for researchers. Among the various whiskers, magnesium oxysulfate whiskers, have been proved to be very suited as an additive for polymers, and they have been paid much attention since they are economically attractive and environmental-friendly materials [3–13].

The synthesis of magnesium oxysulfate whiskers has been reported, especially the synthesis of $5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$. Recently, magnesium hydroxide sulfate hydrate (MHSH) whiskers were systematically investigated by Ding and Ma [11, 14]. Their results indicate that the MHSH whisker would become one of the ideal candidates for flame retardant additives. Lu et al [15] investigated the fire properties of low density polyethylene (LDPE) composites filled with MHSH whisker and microencapsulated red phosphor, and reported that the two flame retardant additives have a synergic effect of flame retardance in the LDPE/MHSH whisker system.

In this paper, the effects of the MHSH whisker content and the addition of zinc stearate as a dispersion additive on the flame retardancy and rheological behavior of the ABS composites were studied.

## Experimental

### *Materials*

ABS (747S) was a commercial product of Qimei Company. MHSH whiskers were provided by Yingkou Weisike Co., China. Zinc stearate was an industrial grade product purchased from Shanghai Reagent Co., China.

### *Composites preparation*

ABS/MHSH composites were prepared by melt compounding of ABS and MHSH whisker in a Rheomix-600 mixer (Haake Rheocord 900, Germany) at 200°C and 60 rpm for 8 min.

The composite compositions are listed in Table 1. All the raw materials were dried at 80°C under vacuum for 24 h before using.

Table 1 Compositions and abbreviation of the prepared composites

| sample abbreviation | ABS ( wt% ) | MHSH ( wt% ) | $ZnSt_2$ |
|---|---|---|---|
| ABS90MHSH10 | 90 | 10 | 0 |
| ABS80MHSH20 | 80 | 20 | 0 |
| ABS70MHSH30 | 70 | 30 | 0 |
| ABS80MHSH20Zn | 80 | 20 | 2% weight of MHSH |

The composites were compression molded into sheets of 1 and 4 mm in thickness at 200°C and 15 MPa for 10 min, followed by cooling to room temperature under a pressure of 12 MPa for structure characterization and property measurements.

### *Evaluation of dispersion of MHSH whisker in ABS resin matrix*

The morphologies of whiskers and the fractured surfaces of composites were observed in a scanning electron microscope (SEM, Hitachi S-2150). The composite specimens were cryo-fractured in liquid nitrogen. The fractured surfaces were coated with a thin layer of gold prior to SEM observations.

*TGA analyses*

All TGA analyses were performed on a Perkin Elmer instruments TGA-7. Samples of 10-12 mg were heated from room temperature to 800°C at a heating rate of 20°C/min under nitrogen.

*Cone calorimetry*

Combustion experiments were performed in a cone calorimeter (Fire Testing Technology Co., UK) at an incident heat flux of $50kW/m^2$.

*Rheological measurements*

Rheological measurements were carried out in an oscillatory mode on a rheometer (Gemini 200 rheometer, Bohlin Co., UK) equipped with a parallel plate geometry using 25 mm diameter plates at 200°C. The samples are 1.0 mm in thickness. In the linear viscoelastic measurements, a small amplitude oscillatory shear (SAOS) was applied, and the dynamic strain scan measurements and the dynamic frequency scan measurements were carried out.

## Results and discussion

*Morphology of MHSH whiskers and composites*

Figure 1 shows an SEM micrograph of MHSH whiskers. This micrograph reveals that MHSH whiskers exhibit fibrous appearance and a large aspect ratio owing to their small diameter. Figure 2 (a, b) shows SEM fractographs of the composites. There is some whisker aggregate in the Figure 2(a), while not in Figure 2(b). The fractographs indicate that the addition of zinc stearate could improve the dispersion of the MHSH whiskers. As a dispersion additive, the addition of zinc stearate could decrease the adhesion between the polymer and filler, so the adhesion between ABS and MHSH in Figure 2(a) was better than that in Figure 2(b), and the MHSH whisker is easier to be pulled out from ABS80MHSH20Zn than ABS80MHSH20.

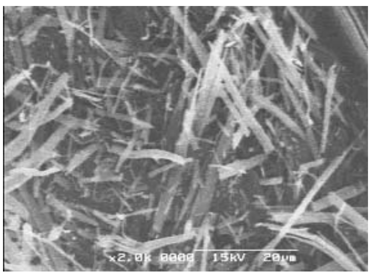
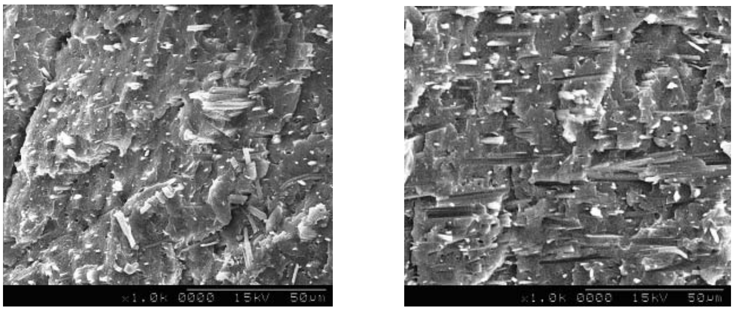



Figure 1 SEM micrograph of an MHSH whisker



(a) (b)

Figure 2 Fractographs of composites: (a) ABS80MHSH20, (b) ABS80MHSH20Zn

*Thermal stability*

Thermal stability is an important property of composites. The kind, size and concentration of filler have great influence not only on the morphology of composites, but also on the thermal stability of it.

The dehydration of $MgSO_4{\cdot}5Mg(OH)_2{\cdot}3H_2O$ is characterized by five stages: [11, 14]

$MgSO_4{\cdot}5Mg(OH)_2{\cdot}3H_2O \rightarrow MgSO_4{\cdot}5Mg(OH)_2{\cdot}2H_2O+H_2O$ (at about 100°C) (1)

$MgSO_4{\cdot}5Mg(OH)_2{\cdot}2H_2O \rightarrow MgSO_4{\cdot}5Mg(OH)_2 +2H_2O$ (at about 310°C) (2)

$MgSO_4{\cdot}5Mg(OH)_2 \rightarrow MgSO_4{\cdot}5MgO+5H_2O$ (from 380°C to 480°C) (3)

$MgSO_4{\cdot}5MgO \rightarrow MgSO_3{\cdot}5MgO+1/2O_2$ (at about 530°C) (4)

$MgSO_3{\cdot}5MgO \rightarrow 6MgO+SO_2$ (over 900°C) (5)

Figure 3, 4 and 5 show the TGA curves and derivative curves of mass loss with respect to temperature (DTG) for the ABS/MHSH composites, MHSH whisker and ABS, respectively. In Figure 3 and 4, The TGA curve of MHSH whisker diplays an apparent several degradation stage in the temperature range from 20°C to 800°C. There are three apparent peaks in DTG curve, peaks at 316°C according to stages (2), peaks at 407°C and 461°C according to stage (3), respectively. As shown in Figure 5, the two main decomposition temperatures at 316°C and 407°C are lower than the ABS decomposition temperature of 436°C.

The thermal stability of the ABS and ABS/ MHSH composites with different MHSH content were compared. Four parameters were measured and listed in Table 2, they are

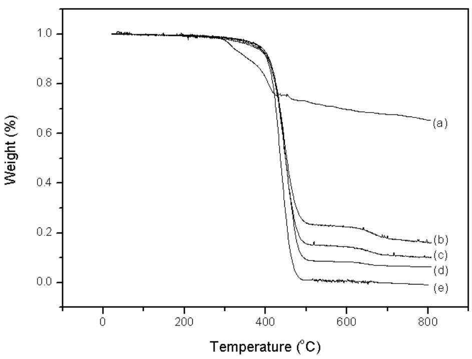



Figure 3 TGA curves of ABS, MHSH whisker and ABS/MHSH composites
(a) MHSH, (b) ABS70MHSH30, (c) ABS80MHSH20, (d) ABS90MHSH10, (e) ABS

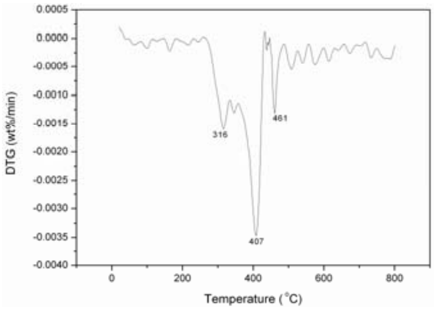



Figure 4 DTG curve of MHSH whisker

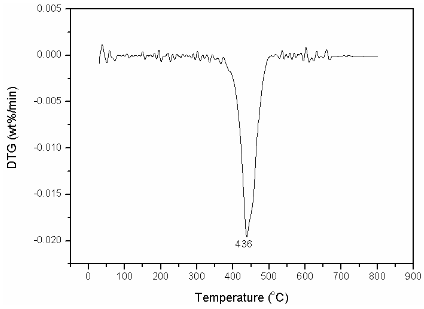



Figure 5 DTG curve of ABS

the 5 wt% loss temperature ($T_{5wt\%}$), the 50 wt% loss temperature ($T_{50wt\%}$), the maximum weight loss temperature ($T_{max}$) and the yield of charred residue at 600°C ($W_{600}$), respectively.

Table 2 TGA results for the thermal degradation of ABS and ABS/MHSH composites

| Sample abbreviation | $T_{5wt\%}$ (°C) | $T_{50wt\%}$ (°C) | $T_{max}$ (°C) | $W_{600}$ (%) |
|---|---|---|---|---|
| ABS | 389 | 441 | 436 | 0.72 |
| MHSH | 317 | / | 407 | 69.1 |
| ABS90MHSH10 | 387 | 449 | 445 | 8.34 |
| ABS80MHSH20 | 370 | 450 | 452 | 14.5 |
| ABS70MHSH30 | 378 | 452 | 442 | 22.4 |

As shown in Figure 3 and Table 2, the $T_{50wt\%}$, $T_{max}$, $W_{600}$ of ABS/MHSH composites are higher than that of ABS. From Table 2, it can be seen that the $T_{50wt\%}$ of ABS90MHSH10, ABS80MHSH20 and ABS70MHSH30 are 8°C, 9°C and 11°C higher than that of ABS, the $T_{max}$ of ABS90MHSH10, ABS80MHSH20 and ABS70MHSH30 are 9°C, 16°C and 6°C higher than that of ABS, respectively. It can also be seen that with increasing MHSH whisker content, the weight of residue increases. The residue of MHSH at 600°C is 69%, so the residues left by MHSH of ABS90MHSH10, ABS80MHSH20 and ABS70MHSH30 at 600°C are 6.9%, 13.8% and 20.7%, respectively; While the total residues of ABS90MHSH10, ABS80MHSH20 and ABS70MHSH30 are 8.34%, 14.5%, 22.4%, respectively, so it can be concluded that the addition of MHSH has increased the residue of ABS. These results indicate that the MHSH content affects the thermal stability of the composites. With increasing MHSH content, the thermal stability of ABS/MHSH composites was improved.

*Flame retardancy*

The reduction of the HRR, and in particular, the peak HRR measured by cone calorimetry has been found to be the most clear-cut evidence of the efficiency of a flame retardant [15].

Figure 6 shows the HRR curves for the ABS and its composites with different MHSH whisker content. The corresponding cone data are presented in Table 3.

It is clear that the reduction in the HRR is different in each of these composites. With increasing MHSH content from 10% to 20%, the peak HRR changes from 584 to

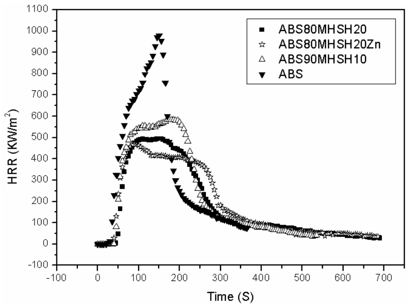



Figure 6 HRR curves for ABS and ABS/MHSH composites

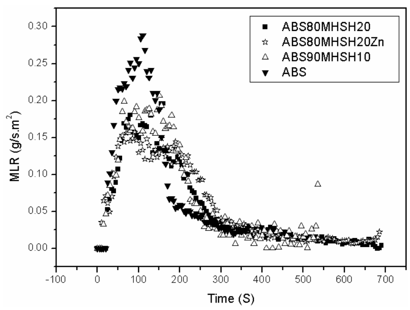



Figure 7 MLR curves for ABS and ABS/MHSH composites

495 KW.m$^{-2}$. Compared to ABS, there is 40% reduction in the peak HRR for the composite containing 10 wt% MHSH whiskers, whereas there are reductions of 50% and 52% for the composites containing 20 wt% and 30 wt% MHSH. These results suggest that the improved flame retardancy of ABS/MHSH composites are greatly dependant on the MHSH whisker content. The composite with zinc stearate has lower HRR than the composite without zinc stearate, indicating the better dispersion of MHSH whisker could improve the flame retardancy of ABS composites.

Table 3 the peak HRR of ABS and ABS/MHSH composites

| Sample abbreviation | Composition(wt%) ABS/MHSH/$ZnSt_2$ | Peak HRR (KW.m$^{-2}$) |
|---|---|---|
| ABS | 100/0/0 | 980 |
| ABS90MHSH10 | 90/10/0 | 584 |
| ABS80MHSH20 | 80/20/0 | 495 |
| ABS80MHSH20Zn | 80/20/2% | 469 |

The MLR of ABS/MHSH composites are significantly lower than that of ABS (Figure 7), which follows the same trend as the HRR data. The consistency of the HRR and the MLR confirms that the flame retardant mechanism of the MHSH whisker depends on a condensed-phase process [15].

As shown in Figure 8, the char residue of ABS/MHSH composites retains its fibrous appearance. So there are two major factors which could enhance the flame retardancy of

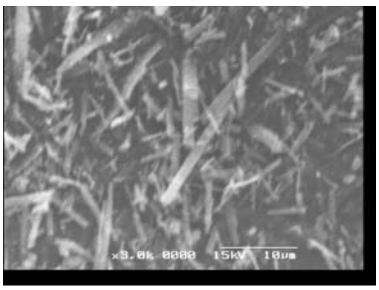


Figure 8 SEM of the char residue of ABS70MHSH30

ABS/MHSH composites. One is the dehydration of MHSH that will remove plenty of heat before the decomposition of ABS and improve the flame retardancy of ABS composites. Another factor is fibrous appearance of the char residue of ABS/MHSH composites, which forms a physical protective barrier on the surface of composites and volatilization might be delayed by the labyrinth effect of the MHSH dispersed in the composites [11, 14].

*Rheological behavior*

Filler should have some influence on the rheological properties of polymer composites, so the measurement of rheological properties is necessary to gain fundamental understanding of the processability and the structure-property relationship for these materials. The curves of the complex viscosity, storage modulus and loss modulus of ABS and its composites are compared in Figure 9-12.

As shown in Figure 9, MHSH whisker content has great influence on the viscosity of composites. With increasing MHSH whisker content, the viscosity of the composites increases significantly at low frequency zone. However, at high frequency zone the viscosity of ABS90MHSH10 become lower than that of ABS, and all the slopes of ABS90MHSH10, ABS80MHSH20 and ABS70MHSH30 are larger than that of ABS. In other word, the viscosity of ABS/MHSH composites decreases more quickly than that of ABS. It is likely because that at high frequency zone, the MHSH were forced to

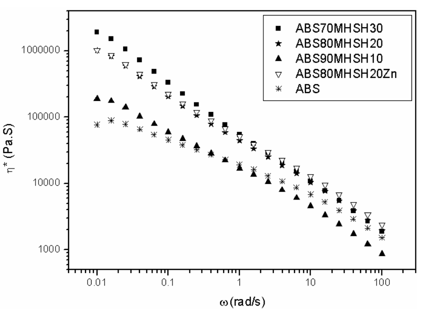



Figure 9 Comparison of complex viscosity of the composites

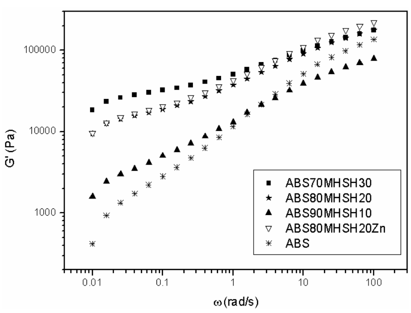



Figure 10 Comparison of storage modulus of the composites

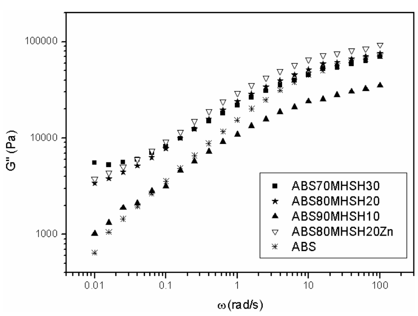



Figure 11 Comparison of loss modulus of the composites

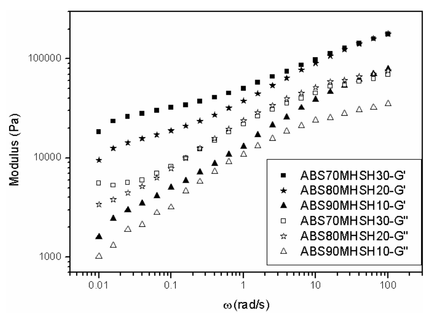



Figure 12 Comparison of storage modulus and loss modulus of ABS/MHSH composites

orient by the shear force, leading to the quickly decrease of viscosity of ABS/MHSH composites.

In Figure 10, with increasing MHSH whisker content, the storage modulus ($G'$) of the composites increases significantly and the $G'$ curves exhibit a more distinct plateau at low frequency zone. It is obvious that with the addition of the MHSH, $G'$ has less strong dependency on $\omega$, $G'$ becomes nearly independent of frequency at low frequency zone, which is characteristic of materials exhibiting solid-like behavior. It was due to the highly anisotropic nature of the fibrous whiskers and simple geometric constraints, the whiskers exhibited local correlations [16, 17]. The lower slope values and the higher absolute values of the dynamic modulus imply the formation of a percolated structure of the dispersed whiskers in the ABS matrix. With such structure, the individual whisker is difficult to rotate freely, and hence the relaxation of this structure is almost completely hindered when imposing small $\omega$. Due to the geometric constraints this type of hindered relaxation of the stacked whiskers would lead to the occurrence of the solid-like behavior observed in ABS/MHSH composites. In summary, owing to the formation of percolation network structure of MHSH whiskers, the incorporation of the MHSH whiskers in ABS matrix leads to a solid-like behavior of the composites, and the modulus and viscosity of the composites increase with the whisker content [16, 18].

As shown in Figure 12, the values of $G'$ of all the ABS/MHSH composites are higher than the values of $G''$ at full frequency zone, and the difference between $G'$ and $G''$ increases with the content of MHSH. This is also an indication of the formation of percolation network or physical jamming [18].

In Figure 9, 10 and 11, the viscosity, storage modulus ($G'$) and loss modulus of ABS80MHSH20Zn are slightly higher than that of ABS80MHSH20, this indicates that the addition of zinc stearate has slight influence on the dispersion of MHSH.

## Conclusions

The flammability characteristics, thermal stability and rheological behavior of ABS/MHSH whisker composites have been investigated. The MHSH content has great influence on the flame retardancy, thermal stability and rheological behavior of composites.

With increasing MHSH whisker content, HRR and MLR of ABS/MHSH composites decrease considerably and $T_{50wt\%}$, $T_{max}$ and $W_{600}$ of the composites increase. The flame retardancy and thermal stability were improved significantly.

With increasing MHSH whisker content, the viscosity, storage modulus of ABS/MHSH composites increase at low frequency zone, and the composites exhibit more distinct solid-like response at terminal zone than ABS. Storage modulus becomes nearly independent of frequency at low frequency zone. The viscosity of ABS/MHSH composites decrease more quickly than that of ABS. It is likely due to the orientation forced by the shear force. The values of $G'$ of all the ABS/MHSH composites are higher than the values of $G''$ at full frequency zone, and the difference between $G'$ and $G''$ increases with the content of MHSH.

The presence of zinc stearate could improve the dispersion of the MHSH whisker in ABS matrix and this leads to slight increase in the viscosity, storage modulus and loss modulus of the composites. The composite with zinc stearate has lower HRR than the composite without zinc stearate, indicating the better dispersion of MHSH whisker could improve the flame retardancy of the composites.

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