

STRUCTURE AND THERMAL PROPERTIES OF EXFOLIATED PVC/LAYERED SILICATE NANOCOMPOSITES VIA IN SITU POLYMERIZATION

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The exfoliated poly(vinyl chloride) (PVC)/montmorillonite (MMT) nanocomposites were synthesized by in situ intercalated polymerization of vinyl chloride (VC) in the presence of organic-intercalated montmorillonite (OMMT). Their structures and thermal properties were characterized. The results showed that layered silicates are well exfoliated and uniformly distributed in PVC matrix during in situ intercalated polymerization of VC in the presence of OMMT. The glass transition temperatures of PVC phases in the PVC/MMT nanocomposites are all lower than that of pristine PVC due to the incorporation of the exfoliated silicate layers in PVC matrix. The 5% mass loss temperature ($T_{5\%}$), the dehydrochlorination temperature ($T_{\max 1}$) of the PVC matrix decreased due to the free and interlayer water in MMT, the low thermal stability, and the enhanced dehydrochlorination of the PVC matrix by alkyl ammonium pre-treated MMT. However, the thermal decomposition temperature of the dehydrochlorinated PVC ($T_{\max 2}$) and char at 600°C are slightly increased in the presence of silicate layers.

Keywords: exfoliation, in situ intercalated polymerization, montmorillonite, poly(vinyl chloride), thermal properties

Introduction

Recently, the polymer/layered silicate nanocomposites have attracted considerable attention owing to their high strength, superior modulus, good heat distortion temperature and superior barrier and flame retardant properties [1–5]. Three approaches have been employed to fabricate polymer/layered silicate nanocomposites, such as in situ polymerization [1], melt compounding [3], and solution blending [6]. In general, in situ polymerization and melt compounding have been proved to be conventional and efficient methods and are widely used to prepare polymer-matrix nanocomposites. In order to obtain the high performance polymer-matrix nanocomposites, one of the key problems is how to get the exfoliated structure of layered silicates in nanocomposites.

Poly(vinyl chloride) (PVC) is now one of the major thermoplastics in the world, and a large amount of PVC is produced worldwide [7]. However, fluid plasticity and thermal stability of PVC are inferior to those of other commodity plastics such as polyethylene and polystyrene [8]. Much improvement of the inferior properties of PVC has been carried out by adding additives such as plasticizer, heat stabilizers, lubricants, fillers and other polymers as well as copolymerization with other monomers [7]. Recently, PVC/montmorillonite (MMT) nanocomposites have been studied. Wang's group prepared the intercalated PVC/MMT nanocomposites by melting compounding [9]. Later, Zhang reported that the addition of liquid epoxy was helpful for MMT in the nanocomposites to be largely intercalated

into PVC matrix, and even exfoliated at high epoxy content (8 phr) [10], which is in accordance with Ishita's results [11]. In the other hand, Wang and his co-worker [12] used tetrahydrofuran (THF) as solvent to blend PVC and MMT, but they still obtained the intercalated nanocomposites. In 2002, the authors [13, 14] firstly prepared the exfoliated PVC/MMT nanocomposites by in situ intercalated polymerization of vinyl chloride (VC) and organic-intercalated MMT. Recently, Gong *et al.* [15] also reported the synthesis of the exfoliated PVC/MMT nanocomposites. Little information is available on their thermal properties. For polymer-matrix composites, there are some relationships between their thermal behaviors and morphological structure, thereby, it is important to investigate the thermal properties of composites [16–18]. In the present work, we focused on characterizing the structure and thermal properties of the exfoliated PVC/MMT nanocomposites.

Experimental

Materials

Sodium montmorillonite (Na-MMT) was supplied by Zhejiang Huate Group Co., China. The Na-MMT has a cation exchange capacity of 100 mequiv./100 g. Vinyl chloride monomer is provided by Wuhan Gedian Chemical Group Co. Ltd., China. Cetyl trimethyl ammonium bromide (CTAB) was analytical reagent. The other compounds were industrial grade products.

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Preparation of organic-intercalated montmorillonite

The organic-intercalated montmorillonite (OMMT) was prepared from Na-MMT and CTAB by ion-exchange reaction according to literature [19]. 80 g Na-MMT was dispersed into 4000 mL deionized hot water (about 80°C) for 30 min by a homogenizer. 30 g CTAB was dissolved in 300 mL water, and the solution was added in dropwise to the above hot Na-MMT and water suspension under vigorous stirring for 2 h to yield white precipitates. In order to ensure the complete removal of bromide ions, the precipitates were washed with deionized hot water till no precipitates of AgBr further formed with 0.1 N AgNO₃ solution. The produced OMMT was dried at 80°C under vacuum up to a constant mass.

Synthesis of PVC/MMT compounded resins

The PVC/MMT compounded resins were synthesized by batch suspension polymerization of vinyl chloride in the presence of OMMT. The reaction apparatus in this work consisted of a stainless steel jacketed reaction vessel of 30-L capacity fitted with four equally spaced stainless steel baffles. The agitator was a four-flat-blade turbine. The reaction mixture consisted of liquid VC as the dispersed phase and deionized water as the continuous phase. The reaction pressure and temperature were 3 MPa and 54°C ($\pm 0.2^\circ\text{C}$), respectively. Poly(vinyl acetate) (PVA) and hydroxyl propyl cellulose (HPC) were used as suspending agents. The initiator was the mixture of azobisisobutyronitrile (AIBN) and 2-ethylhexyl peroxydicarbonate (EHP). After the conversion of VC is up to 85%, the polymerization ended, and the PVC/MMT compounded resins with average particle size of 150 μm containing 0, 2.5, 5.0 and 7.5 mass fraction (%) of OMMT were obtained.

Preparation of PVC/MMT nanocomposites

The pristine PVC and PVC/MMT nanocomposites with same composition of the stabilizer and processing additives were plasticized by a two-roll mill at 180°C for 10 min. The molded plates with dimensions of 200×80×3.2 mm were compression molded at 175°C for 8 min, with a 5 min preheating period. Care was taken at this stage to ensure precise timing so as to eliminate any differences that might arise as a result of the samples having different thermal histories.

Small angle X-ray diffraction (SAXD) measurements

A Philips X'Pert X-ray Diffractometer with CuK α radiation ($\lambda=1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 30 mA was used to study the diffraction behavior of MMT and PVC/MMT nano-

composites. All experiments were carried out in the reflection mode at ambient temperature with 2θ varying between 1 and 10°. The scanning speed was 1° min⁻¹ and the step size was 0.01°.

Morphology observations

The specimens of PVC/MMT nanocomposites for transmission electron microscope (TEM) observation were ultramicrotomed to give 60 nm-thick sections with a diamond knife under liquid nitrogen environment using a Reichert-Jung Ultracut E microtome. Sections were collected on 300 mesh copper TEM grids and subsequently dried with filter paper, and examined by a Hitachi-800 TEM at an accelerating voltage of 22 kV.

Differential scanning calorimetry (DSC)

DSC measurements were conducted in a TA2910 Instrument DSC analyzer at a heating rate of 10°C min⁻¹ under dry nitrogen atmosphere with the flow rate of 25 cm³ min⁻¹. The experimental temperature range was from -20 to 130°C.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was conducted with a TA2980 instrument dynamic mechanical analyser at a fixed frequency of 10 Hz and oscillation amplitude of 0.15 mm. The temperature range studied was from -20 to 130°C with a heating rate of 2°C min⁻¹.

Thermogravimetry analysis (TG)

The thermal degradation characteristics of the PVC/MMT nanocomposites were carried out using a Seiko thermogravimetric analyser (model SSC/5200). The mass loss vs. temperature was measured at a heating rate of 10°C min⁻¹ in helium atmosphere from 50 to 600°C.

Results and discussion*Exfoliation of organic-intercalated MMT in PVC/MMT nanocomposites*

Figure 1 is the SAXD spectra of Na-MMT and OMMT. There is a diffraction peak at $2\theta=4.405^\circ$ in OMMT SAXD curve, corresponding to a basal spacing (d_{001}) of 2.0 nm, much higher than 1.5 nm of pristine Na-MMT. The enlarged intra-gallery of OMMT due to intercalation of the alkyl ammonium surfactant indicates the decrease of electrostatic interaction between adjacent clay layers and provides a good opportunity for macromolecular chains to diffuse into

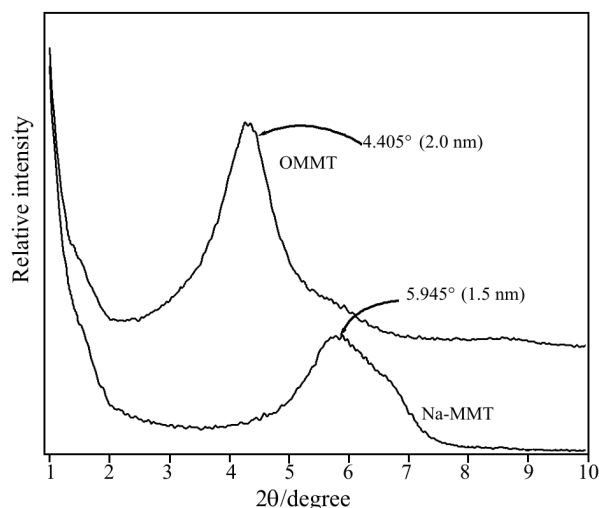


Fig. 1 SAXD spectra of Na-MMT and OMMT

the intra-galleries during the following in situ polymerization of VC monomers.

Figure 2 shows the SAXD spectra of PVC/MMT composites synthesized by in situ intercalated polymerization of VC in the presence of OMMT. Obviously, there is not Bragg diffraction peaks in SAXD spectra of PVC/MMT composites with different contents of OMMT. It indicates that the monomers of VC enter into the space of layered organic-intercalated MMT, and produce the exfoliated PVC/MMT nanocomposites.

Figures 3a and b are TEM micrographs of PVC/MMT nanocomposites with 5 and 7.5 mass fraction (%) OMMT. We can see clay layers are almost exfoliated into individual layers, and the exfoliated MMT layers are dispersed in PVC matrix as the nano-sized scale. The micro-sized domains are proven to be some impurities and stabilizers, such as plumb stearate [20]. These results prove that the layered silicates are well exfoliated and uniformly distributed in PVC matrix, and the exfoliated PVC/MMT nanocomposites are formed during in situ intercalated polymerization of VC in the presence of OMMT.

Glass transition temperature of PVC in PVC/MMT nanocomposites

Figures 4 and 5 present the DSC and DMA curves ($\tan\delta-T$) for PVC and PVC/MMT nanocomposites. The glass transition temperatures (T_{go} at onset point for DSC, and T_{gp} at peak point for DMA) of PVC phases in pristine PVC and PVC/MMT nanocomposites are listed in Table 1. It is one interesting phenomenon that the glass transition temperature of PVC phases in the PVC/MMT nanocomposites is lower than that of pristine PVC. It is in accordance with Liu *et al.*'s result that the glass transition temperature of polypropylene (PP) phase in the PP/MMT nanocomposite decreased in the presence of the silicate layers [21].

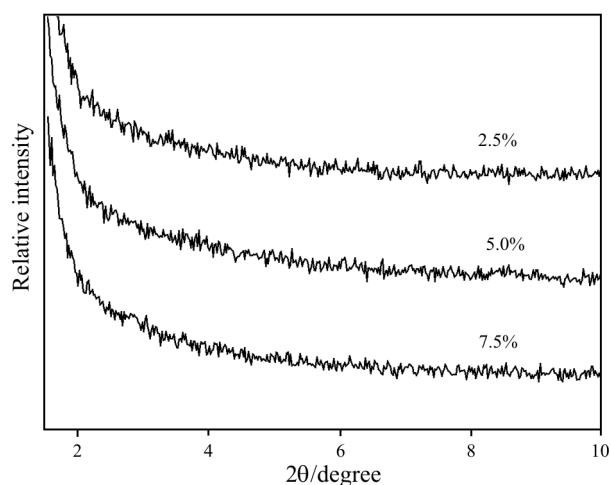


Fig. 2 SAXD spectra of PVC/MMT composite with different loading of OMMT

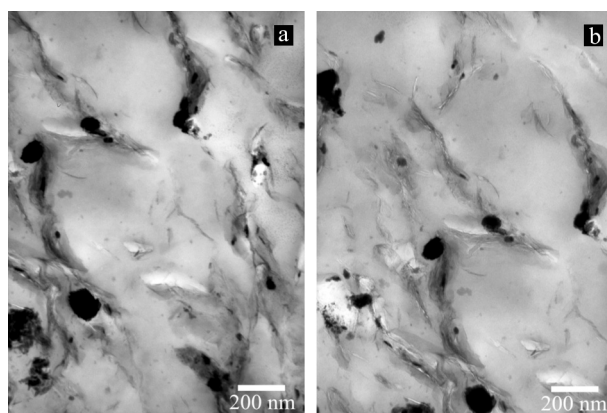


Fig. 3 TEM micrograph of PVC/MMT nanocomposite with a – 5 mass fraction (%) and b – 7.5 mass fraction (%) OMMT

We think that the exfoliated MMT layers dispersed in PVC matrix as nano-sized scale maybe keep PVC macromolecules apart, and decrease the intermolecular interaction between PVC macromolecules in nanocomposites. Thereby, it leads to the decrease of the glass transition temperature of PVC phases in the PVC/MMT composites. Ash's research group [22] also reported that the presence of nano-sized alumina particles decreased the glass transition temperature of polymethylmethacrylate (PMMA) phase in the

Table 1 T_g of PVC phases in PVC and PVC/MMT nanocomposites

Sample	$T_{go}/^{\circ}\text{C}$ (DSC method)	$T_{gp}/^{\circ}\text{C}$ (DMA method)
Pure PVC	69.3	83.6
PVC/2.5% MMT	68.4	79.6
PVC/5.0% MMT	64.9	79.2
PVC/7.5% MMT	65.2	80.1

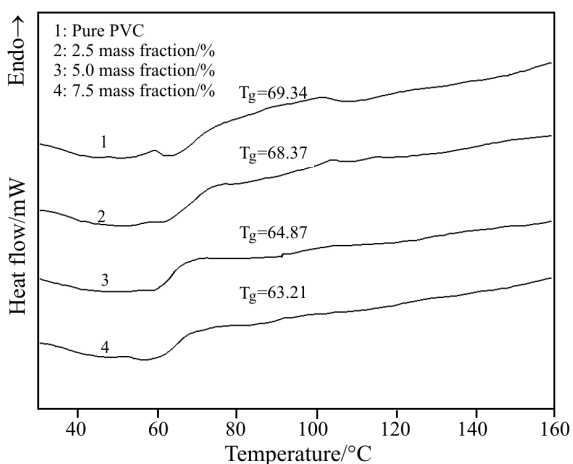


Fig. 4 DSC heating curves for PVC and PVC/MMT nanocomposites

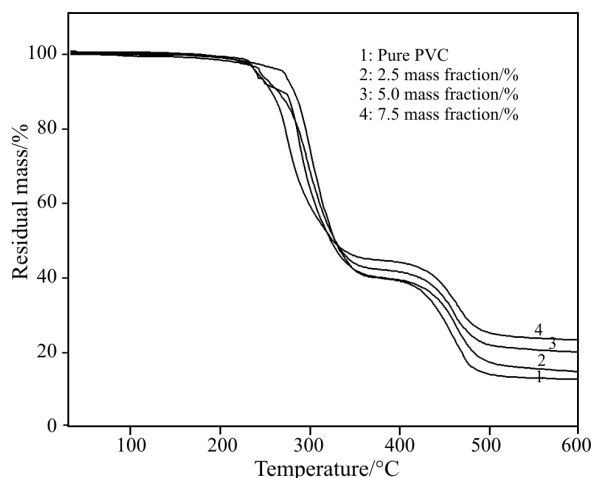


Fig. 6 TG curves for the pristine PVC and nanocomposites with different loading of OMMT

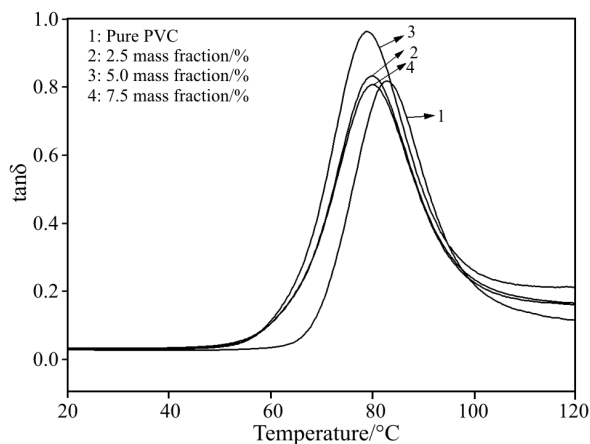


Fig. 5 Variation of $\tan\delta$ with temperature for PVC and PVC/MMT nanocomposites with different loading of OMMT

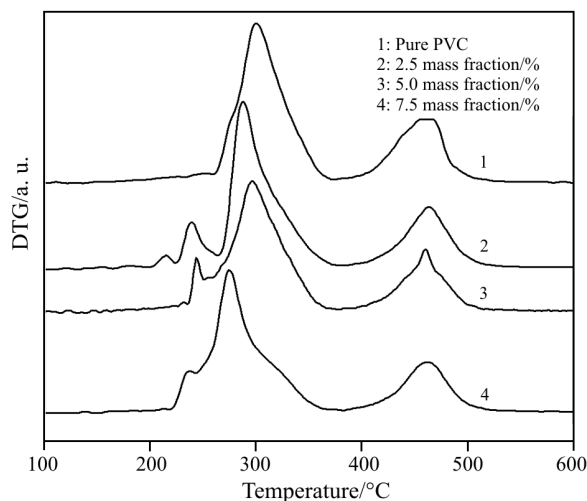


Fig. 7 DTG curves for the pristine PVC and nanocomposites with different loading of OMMT

PMMA/alumina nanocomposites due to interaction of polymer with the filler particles. The mechanism how the presence of nano-sized particles or silicate layers decreases the glass transition temperature of polymer-matrix nanocomposites needs to be studied further.

Thermogravimetric analysis (TG)

Figures 6 and 7 show the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the pristine PVC and nanocomposites. These mass loss curves exhibit two flat regimes in the testing temperature range. It is evident that the two stages corresponding to the dehydrochlorination (250~350°C) of the PVC matrix and to the thermal decomposition (400~470°C) of the dehydrochlorinated PVC, which consists mainly of conjugated double bonds [23]. Thereby, there are two maximum loss temperatures (T_{max1} and T_{max2} , defined as the peaks in the DTG curve) in these curves.

From the above curves, the 5% mass loss temperature ($T_{5\%}$), maximum mass loss temperatures (T_{max1} and T_{max2}) and char at 600°C can be obtained and are listed in Table 2. It can be seen that both $T_{5\%}$ and T_{max1} are decreased, whilst T_{max2} and char at 600°C are slightly increased in the presence of silicate layers. Why $T_{5\%}$ of PVC/MMT nanocomposites decreases is related to the low thermal stability of alkyl ammonium pre-treated MMT. It is related to that the organic quaternary ammonia salt used for treating

Table 2 TG results of PVC and PVC/MMT nanocomposites

Sample	$T_{5\%}/$ °C	$T_{max1}/$ °C	$T_{max2}/$ °C	Char at 600°C/%
Pure PVC	270.6	300.3	455.5	12.6
PVC/2.5% MMT	236.5	287.6	465.3	14.7
PVC/5.0% MMT	236.4	296.3	460.4	19.8
PVC/7.5% MMT	236.0	275.0	460.3	23.1

clay is easy to be thermally decomposed, and decreases the thermal stability of organic-intercalated MMT [24]. In the other hand, there is a strong interaction between the chloride in PVC and the quaternary ammonium cation ions in OMMT. Thereby, the OMMT acts as a catalyst to enhance the dehydrochlorination of the PVC matrix, and leads to decrease in $T_{\max 1}$. However, it should be mentioned that $T_{\max 2}$ and char at 600°C are slightly increased in the presence of silicate layers. It is because that these exfoliated silicate layers in PVC matrix act as a barrier to minimize the permeability of volatile degradation products out of the material during the thermal decomposition of the dehydrochlorinated PVC, which consists mainly of conjugated double bonds. The results are significant to improve their flame retardant and ablative properties.

Conclusions

Based on the outcomes and results obtained in this study, we can draw some definitive conclusions. The exfoliated PVC/MMT nanocomposites were synthesized by in situ intercalated polymerization of vinyl chloride (VC) in the presence of OMMT. The glass transition temperatures of PVC phases in the PVC/MMT nanocomposites are all lower than that of pristine PVC due to the incorporation of the exfoliated silicate layers in PVC matrix. The 5% mass loss temperature ($T_{5\%}$) and the dehydrochlorination temperature ($T_{\max 1}$) of the PVC matrix decreased due to the free and interlayer water in MMT, the low thermal stability and the enhanced dehydrochlorination of the PVC matrix by alkyl ammonium pre-treated MMT. However, the thermal decomposition temperature of the dehydrochlorinated PVC ($T_{\max 2}$) and char at 600°C are slightly increased in the presence of silicate layers.

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References

- 1 Y. Q. Zhang, J. H. Lee, J. M. Rhee and K. Y. Rhee, *Compos. Sci. Technol.*, 64 (2004) 1383.
- 2 F. L. Gong, C. G. Zhao, M. Feng, H. L. Qin and M. S. Yang, *J. Appl. Polym. Sci.*, 39 (2004) 293.
- 3 J. W. Cho and D. R. Paul, *Polymer*, 42 (2001) 1083.
- 4 P. Ganan and I. Mondragon, *J. Therm. Anal. Cal.*, 73 (2003) 783.
- 5 J. W. Gilman, *Appl. Clay Sci.*, 15 (1999) 31.
- 6 Y. H. Hyun, T. L. Lim, H. J. Choi and M. S. John, *Macromolecules*, 34 (2001) 8084.
- 7 K. Endo, *Prog. Polym. Sci.*, 27 (2002) 2021.
- 8 R. C. Stephensen and P. V. Smallwood, *Encyclopedia of Polymer Science Engineering*, 2nd Ed., John Wiley & Sons, New York 1989, p. 843.
- 9 D. Y. Wang, D. Parlow, Q. Yao and C. A. Wilkie, *J. Vinyl Add. Technol.*, 8 (2002) 139.
- 10 C. Y. Wan, X. Y. Qiao, Y. Zhang and Y. X. Zhang, *J. Appl. Polym. Sci.*, 89 (2003) 2184.
- 11 H. Ishida, S. Campbell and J. Blackwell, *Chem. Mater.*, 12 (2000) 1260.
- 12 D. Y. Wang and C. A. Wilkie, *J. Vinyl Add. Technol.*, 8 (2002) 238.
- 13 Q. X. Liu, X. P. Zhou, X. L. Xie, C. S. Wang and C. D. Li, *Poly(vinyl chloride)*, 2 (2002) 1.
- 14 Q. X. Liu, X. P. Zhou, X. L. Xie, K. L. Fung, R. K. Y. Li and Y.-W. Mai, *IUPAC World Polymer Congress 2002, 39th International Symposium on Macromolecules*, July 7–12, Beijing, China 2002, p. 669.
- 15 F. L. Gong, C. G. Zhao, M. Feng, H. L. Qin and M. S. Yang, *J. Mater. Sci.*, 39 (2004) 293.
- 16 X. L. Xie, K. Aloys, X. P. Zhou and F. D. Zeng, *J. Therm. Anal. Cal.*, 74 (2003) 317.
- 17 R. D. Sweeting and X. L. Liu, *Composites*, 35 (2004) 933.
- 18 V. M. Fonseca, V. J. Fernandes, A. S. Araujo, L. H. Carvalho and A. G. Souza, *J. Therm. Anal. Cal.*, 79 (2005) 429.
- 19 M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada, *Macromolecules*, 30 (1997) 6333.
- 20 X. L. Xie, R. K. Y. Li, Q. X. Liu and Y.-W. Mai, *Polymer*, 45 (2004) 2793.
- 21 X. H. Liu and Q. J. Wu, *Polymer*, 42 (2001) 10013.
- 22 B. J. Ash, L. S. Schadler and R. W. Siegel, *Mater. Lett.*, 55 (2002) 83.
- 23 Y. Z. Meng and S. C. Tjong, *Polymer*, 40 (1999) 2711.
- 24 W. Xie, Z. M. Gao, K. L. Liu, W. P. Pan, R. Vaia, D. Hunter and A. Singh, *Thermochim. Acta*, 367–368 (2001) 339.

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