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Research progress on the flame retardation and modification of polypropylene by montmorillonite

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Abstract. Montmorillonite can be used to achieve nano-dispersion level by forming peel or intercalation structure in polypropylene body, so as to improve the mechanical properties of the material. In addition, montmorillonite plays the role of nucleating agent during the crystallization of polypropylene, which improves the crystallization efficiency of polypropylene. After the organic modification of montmorillonite, the spacing between crystal surfaces can be enlarged to form organic montmorillonite, which makes the molecular chains of polypropylene more easily dispersed to the interlayer of organic montmorillonite, forming a dense surface layer in the process of thermal decomposition, so as to improve the thermal stability of polypropylene and enhance the flame retardant property of polypropylene. Many previous studies have shown that montmorillonite plays a significant role in improving the mechanical strength and crystallization effect of polypropylene, as well as the flame retardant properties of nanocomposites.

Keywords: Montmorillonite, Polypropylene, Tensile Strength, Crystallization, Flame Retardancy.

1. Introduction

Polypropylene is a kind of non-toxic, odorless, tasteless milky white high crystallization polymer, because of its high crystallinity, structure is relatively regular, so polypropylene has good mechanical properties, polypropylene is widely used in various fields of life. However, polyolefins are less effective as flame retardants, so some flame retardants are needed to prevent the burning of polypropylene. Expandable flame retardants are widely used in flame retardant polyolefin materials because of their halogen-free and environmental protection characteristics. But flame-retardant polyolefin with expansion flame retardant has a certain effect on the mechanical structure. For example, if pentaerythritol ester melamine salt is used to flame retardant polypropylene, the tensile strength and notched impact strength of flame retardant polyolefin will be slightly reduced [1, 2].However, according to the research of Paul et al system on the impact resistance of elastomer and nano-clay modified polypropylene [1], the impact strength of polypropylene composite is increased by 10-20 times when the content of ethylene - octene elastomer is 30% and that of montmorillonite is 5% [3].It can be seen that montmorillonite is helpful to improve the impact resistance of polypropylene. On the other hand, the flame retardants of polypropylene/expansive flame retardant/organic montmorillonite/polyolefin elastomer composites have been characterized by limiting oxygen index and vertical combustion experiment. When the content of montmorillonite is 0% ~ 2%, the limiting oxygen index increases with the increase of the content of montmorillonite, and when the content of montmorillonite reaches 2%, its limiting oxygen index value also reaches the maximum. That's 29.3%. It can be seen that montmorillonite greatly improves the flame retardant performance of polypropylene/expansive flame retardant composites [3].

Based on the above content, this paper mainly introduces the improvement of tensile strength of polypropylene by montmorillonite, the influence of montmorillonite and compatibilizers on crystallization of polypropylene, and the flame retardant performance of polypropylene by montmorillonite, as well as the current research progress and future development prospects of this material.

2. Performance improvement of polypropylene composite modified by nano montmorillonite

2.1. Structure and properties of montmorillonite

Montmorillonite, or micrystalline kaolinite, is a natural mineral of silicate that is the main mineral component of bentonite ore. It includes Al_2O_3 16.54%; MgO 4.65%; SiO_2 50.95%. The structural formula is (Al, Mg)$_2$ [SiO_{10}] $(OH)_2 \cdot nH_2O$. Monoclinic crystal system, many micrystalline, aggregate is like soil, spheroid and so on. White microstrip light gray, containing impurities is light yellow, light green, light blue, earth like luster or no luster, there is a sense of slip. When water is added, it expands several times in volume and turns into a paste. The volume shrinks after heat and dehydration. It has strong adsorption capacity and cation exchange performance. It is mainly produced in the weathering crust of volcanic tuff. Montmorillonite (including calcium base, sodium base, sodium-calcium base, magnesium base montmorillonite) has been peeled and dispersed, purified and modified, ultra-fine classification, and special organic composite. The average wafer thickness is less than 25nm, and it can be used as bleach and adsorbent filler, so it is known as "universal material". The organic cationic modified montmorillonite (OMMT) is oleophilic, and can be stripped into nanoscale lamellar structure during mixing with monomer or polymer melt, which is uniformly dispersed in the polymer monomer, thus forming nanocomposite materials.

2.2. Preparation of nano montmorillonite modified polypropylene composites

The improvement of the properties of PP/MMT nanocomposites is related to the dispersion level and the interaction between the MMT laminates and the polymer matrix. Therefore, it is of great significance to improve the compatibility between them. Melt blending and intercalation polymerization are the main methods to prepare PP/MMT. The fusion intercalation method can be used in general composite processing equipment and has broad industrial prospect. The properties of the composites can be changed by modifying MMT or grafting PP to improve their compatibility.

2.3. Introduction of montmorillonite to the enhancement of polypropylene tensile strength

Commonly used plastic raw material for polypropylene, due to its rich source, cheap price, strong heat resistance, safe and harmless characteristics, is widely used in a variety of daily necessities manufacturing raw materials. But polypropylene also has poor mechanical strength, toughness and hardness are not very high defects, people have been committed to improving the toughness of polypropylene, which is also a very hot topic in the polymer field [4]. In the organic/inorganic nanomaterial system of polypropylene, montmorillonite can form a peel or intercalation structure in the polypropylene body, so as to achieve the nano dispersion level. Thus, mechanical properties of materials can be improved [4]. In the preparation of PP/OMMT nanomaterials, polypropylene is inserted between montmorillonite lamellae to destroy the lamellae structure of montmorillonite, so that the lamellae with a thickness of nanoscale are dispersed in polypropylene, and nano composite is realized between them [5]. This can further enhance the interface interaction between the two, so that the impact strength of the composite material, material hardness, tensile properties and other mechanical properties compared with pure polypropylene have been greatly improved. This provides more space for nanocomposites to better replace other materials [6].

In order to prove through experiments that montmorillonite can enhance the mechanical strength of polypropylene, Chen Kui et al. used S800 powder as raw material to make polypropylene, and OMMT1 (TJ-2, quaternary ammonium type) and OMMT2 (KH-V6, organic ammonium type) were used for organic montmorillonite. Polypropylene and montmorillonite were mixed in GH-100Y high speed mixer with different proportions, and then melted and mixed by ZSE-34 twin screw extruder and granulated to formulate a certain content of OMMT. Finally, the standard spline was injected into SZ100/800 injection molding machine.

In terms of performance testing, the team tested V-notch impact strength on XJU-5.5 cantilever beam impact tester in accordance with GB/T 1843-1996 standards. The diameter of indenter was 5mm and the test load was 613N. The average value of 5 tests was taken as the result.

The results of mechanical properties are shown in Figure 1. The hardness curve of PP/OMMT nanocomposites varies with the mass fraction of OMMT1 and OMMT2.As can be seen from the figure, compared with general polypropylene, the hardness of OMMT1/PP and OMMT2/PP composites increased by 11% and 19%, respectively. FIG.(c) and FIG. (d) show the mechanical properties of PP/OMMT nanocomposites as a function of the mass fraction of OMMT1 and OMMT2. It can be seen from the figures that both montmorillonite have good toughening effect on the polypropylene matrix, and the impact resistance of the two materials is increased by 18% and 20% respectively.

FIG 1.(a) and (b) show the test results of mechanical properties,(c) and (d) show the mechanical properties of PP/OMMT nanocomposites as a function of the mass fraction of OMMT1 and OMMT2 FIG1.shows the mechanical properties and the mechanical properties of PP/OMMT nanocomposites.

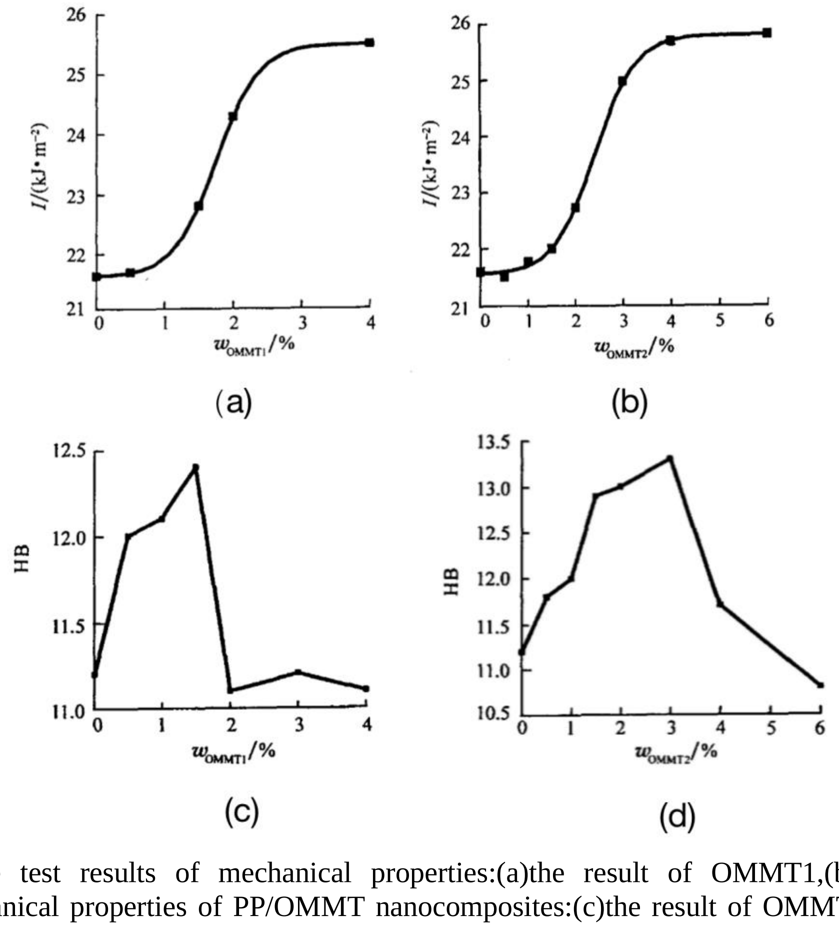

Figure 1. The test results of mechanical properties:(a)the result of OMMT1,(b)the result of OMMT2.mechanical properties of PP/OMMT nanocomposites:(c)the result of OMMT1,(d)the result of OMMT2.

2.4. Influence of montmorillonite on polypropylene crystallization

The crystallization process of polymer can directly affect the physical properties of polymer. The crystallization of polymer has become an important process in scientific research experiments. In recent years, the research on the properties of organic montmorillonite/polypropylene composites has been gradually developed. Many experiments have shown that montmorillonite can significantly improve the crystallization properties of polypropylene materials. According to previous experiments, montmorillonite plays the role of nucleating agent during the crystallization of polypropylene, which improves the crystallization efficiency of polypropylene [7].

Dai Xin et al. prepared β-i PP by loading β-nucleating agent on particle surface and prepared β-nucleating MMT (β-MMT). The effects of different factors on the crystallinity and β-crystal content of i PP/β-MMT nanocomposites were discussed.

The following figure shows the crystal peak temperature (c) and β-crystal content (d) of i PP / β-MMT nanocomposites (PN10 and PM10) prepared by dry and wet methods as a function of MMT content. As can be seen from FIG. 2, although the crystallization peak temperature of β-MMT filled i PP nanocomposites prepared by dry and wet methods increased with the increase of the amount of β-MMT, the variation law was different. When the amount of β-MMT was 1wt %, the iPP crystallization peak temperature increased from 114.5°C to 117.3°C, and the K_β value was about 0.34. The crystallization peak temperature and K_β value increased significantly with the increase of β-MMT content. The crystallization peak temperature of PN10 nanocomposites is 122.4°C, and the K_β value is close to 1.00, which shows that the β-MMT prepared by dry method has a high enough β-nucleation when MMT/HA =1000/1.In conclusion, increasing the content of β-MMT can increase the crystallization peak temperature and β-crystal content, but the effect is affected by the mass composition ratio of MMT/HA and the preparation method.

FIG 2. shows the crystal peak temperature and the β-crystal content.

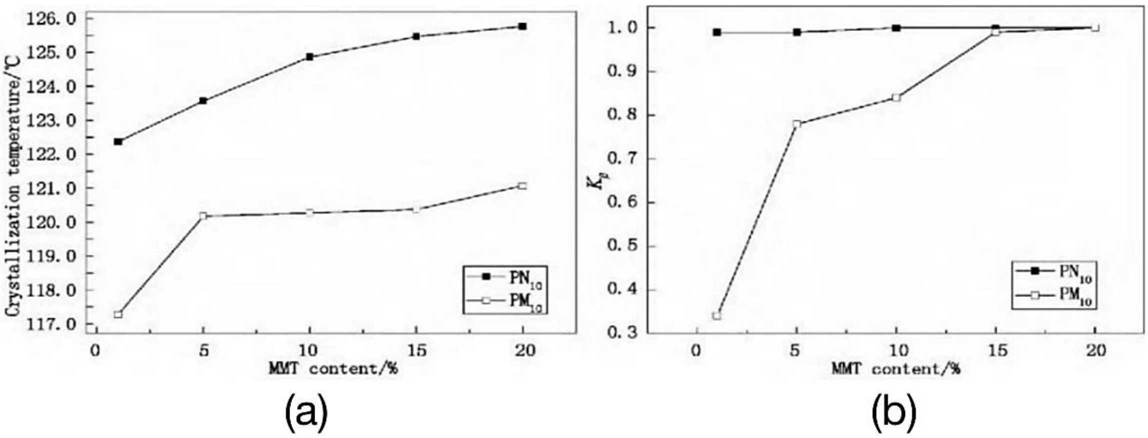

Figure 2. Measurement result: (a) The crystal peak temperature, (b)The β-crystal content.

3. Introduction of montmorillonite for improving flame retardancy of polypropylene/expansive flame retardant composites

Polypropylene is a kind of general polymer material. However, its low thermal stability and poor flame retardancy greatly limit the application of PP. Flame retardants are usually added to PP to improve its flame retardancy. In the process of PP combustion, the hydrogen halide produced by halogen flame retardant reacts with the free radical generated by the thermal decomposition of PP, blocking the thermal decomposition of PP and improving the flame retardant property of PP. But halogenated flame retardants pose potential hazards to humans and the environment, limiting their use. Compared with halogenated flame retardants, intumescent flame retardants (IFRs) are halogen-free flame retardants which prevent or delay PP combustion by forming dense carbon layer through expansion. Their characteristics of microtoxicity and good flame retardancy make them rapidly recognized in recent years. In addition, people have tried to add montmorillonite (MMT) to PP for flame retardant modification, but the results show that the flame retardant performance of PP is not significantly improved, but after organic modification of MMT, the spacing between crystal surfaces becomes larger, forming organic montmorillonite (OMMT). The PP molecular chain is more easily dispersed to the interlayer of OMMT, forming a dense surface layer in the process of thermal decomposition, thus improving the thermal stability of PP and enhancing the flame retardant property of PP.

Chen Shubao et al. dried PP, OMMT and IFR in the oven at 80℃ for 4h, and then added the compatibilizer dimethyl silicone oil to evenly mix, melt and blend before granulating [8]. After drying the particles in the oven at 80℃ for 4h, the particles are injected into standard samples by injection molding machine. The ratio of PP/IFR/OMMT composite material is shown in the following figure:

Table 1. The ratio of PP/IFR/OMMT composite material.

Number	Sample	IFR/%	OMMT/%	PP/%
1	PP/IFR（10%）/OMMT（0%）	10	0	90
2	PP/IFR（10%）/OMMT（2%）	10	2	88
3	PP/IFR（10%）/OMMT（5%）	10	5	85
4	PP/IFR（10%）/OMMT（10%）	10	10	80
5	PP/IFR（10%）/OMMT（15%）	10	15	75
6	PP/IFR（15%）/OMMT（0%）	15	0	90
7	PP/IFR（15%）/OMMT（2%）	15	2	88
8	PP/IFR（15%）/OMMT（5%）	15	5	85
9	PP/IFR（15%）/OMMT（10%）	15	10	80
10	PP/IFR（15%）/OMMT（15%）	15	15	75
11	PP/IFR（20%）/OMMT（0%）	20	0	90
12	PP/IFR（20%）/OMMT（2%）	20	2	88
13	PP/IFR（20%）/OMMT（5%）	20	5	85
14	PP/IFR（20%）/OMMT（10%）	20	10	80
15	PP/IFR（20%）/OMMT（15%）	20	15	75

The team conducted oxygen index (LOI) test with the ultimate oxygen index tester, and the results showed that the flame retardant properties of PP/IFR/OMMT composites changed as shown in Figure 1.As can be seen from the figure, when OMMT is not added, LOI of PP/IFR composite material increases from 17.5% to 20.5% with the increase of IFR filling amount. When mixed with OMMT of different mass fractions, LOI further increased with the increase of OMMT filling amount, and LOI of sample 8 increased from 18% to 26%, indicating that OMMT and IFR had obvious synergistic flame retardant effect. When the OMMT filling was increased to 15%, the LOI of sample 10 was 28%. It can be seen that excessive OMMT does not significantly increase the LOI of composite materials, but tends to be flat. Therefore, when the content of OMMT is within a certain range, the flame retardant performance of PP/IFR composites can be improved to a certain extent [8].

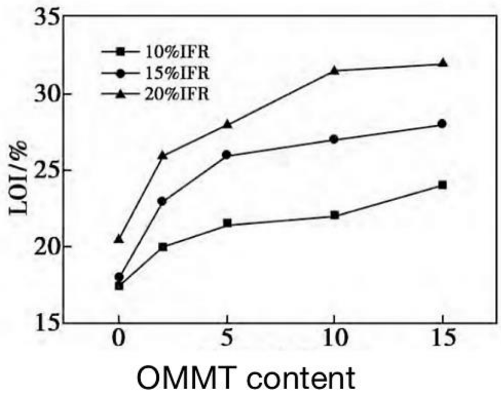

Figure 3. shows the flame retardancy of PP/IFR/OMMT composites.

4. Conclusion

To sum up, polyolefin has a wide range of applications in daily life. Since the introduction of montmorillonite to modify polypropylene can greatly improve the tensile strength of polyolefin materials, this composite material is highly likely to become the main direction of optimizing polypropylene in future production. In terms of flame retardant, compared with the traditional expansive flame retardant, after adding montmorillonite, the synergistic action with the expansive flame retardant can greatly improve the flame retardant ability of the material. And because montmorillonite has the characteristics of cheap price, low economic cost, non-toxic and harmless, it may become the main flame retardant polypropylene material in the future.

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