

# Energy Storage and Flame Retardance of Building Organic Composites

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The study is to understand the energy storage and flame resistance of architectural organic composites by dealing with molecular design of phase change energy storage thermal infrared interference materials. In this stage, the molecular design of phase change energy storage thermal infrared interference materials and the dehydration pretreatment of raw materials are carried out. The results of orthogonal design and flame resistance test are verified, and the results show that the flame resistance is good. Conclusion has been drawn that CGCP is an effective energy storage and flame resistance material.

## 1. Introduction

Along with the increasing demand for architectural engineering in modern society, how to improve the performance of buildings has become the focus discussed among the people. At present, in order to meet the needs of people, most architectural engineering will use organic composites which can provide higher energy storage and flame resistance so as to realize the fire-resistant capacity of houses, as well as to store and use thermal energy to achieve the purpose of energy conservation and environment protection.

This study focuses on a new kind of phase change energy storage flame resistance composite. The temperature control function of the energy storage fiber, the interference of infrared wave, the flame resistance ability and the moisture absorption and permeability of the composite are analyzed and investigated. In the study, diphenylmethane diisocyanate (MDI), polyethylene glycol (PEG), and 1, 4-butanediol (BDO) are used as the main raw materials to prepare polyurethane (PU) phase change energy storage thermal infrared interference material with good dispersity. The relationship between molecular weight and phase change temperature of PEG is analyzed from curve fitting. The phase change performance of PEG with different molecular weight is studied and the most suitable molecular weight of PEG is determined. Finally, it is confirmed that the material has good usability. The results of orthogonal design and flame resistance test are verified, and the results show that the flame resistance is good. Conclusion has been drawn that CGCP is an effective energy storage and flame resistance material.

## 2. Literature review

At present, the flame-retarding of polypropylene is mainly the process of grafting the main flame-retardant element in the synthesis process of polypropylene, that is, the structural flame-retardant of PP. The flame-retardant properties are imparted to the PP by adding flame retardants and certain flame-retardant materials to the PP material. According to the action mechanism of the flame retardant, the flame retardant can be divided into two types of reactive flame retardant and additive flame retardant. Additive flame retardants are generally more convenient. Research and application are extensive. The types of additive flame retardants can be mainly divided into the following categories (Dasari et al., 2013).

Halogen-based flame retardants are the most studied and used chemical flame retardants in the world today. The most widely used are chlorine-containing or bromine-containing flame retardants. However, when it is burned, it generates a large amount of smoke. At the same time, it releases a large amount of toxic and corrosive gases, poses a great threat to life safety, and severely pollutes the environment. With the increasing

attention to environmental problems and the improvement of this kind of flame retardant, the research and development of low-smoke halogen-free flame retardants are imminent (Khadiran et al., 2015).

Hydrotalcite-like (LDHS) is also commonly referred to as anionic clay, and it is also one of the hot topics for polymer materials workers in recent years. The main reason is that LDHs themselves have very unique properties. It shows a broad application prospect in the fields of catalysis, environmental protection, and biomedicine. LDHs is a double hydroxyl metal hydroxide composed of positive metal hydroxide laminates and interlayer anions, the hydroxyl groups on the laminates and the crystalline water between layers. This special layered structure and composition makes the water vapor released during thermal decomposition absorbs a large amount of heat, thereby reducing the temperature of the whole combustion system and diluting the combustible gas. The interlayer divalent and trivalent metal ions are the active components of smoke elimination. The substances produced by LDHs decomposition are mostly alkaline porous materials, with a larger specific surface, which can adsorb toxic and harmful gases, especially acid gases (Chung et al., 2014). With the development of nano-flame-retarding technology and nano-composite materials, the nano-composite principle and technology have been successfully introduced in the field of polymer flame-retardant. The combination of the two provides a new development idea for the development of flame-retardant technology, and has quickly become an important research direction in the field of flame retardant. In the past two decades, many researchers have conducted systematic studies on the thermal stability and flame-retardant properties of polymeric flame-retardant materials such as polymer layered montmorillonites and layered double hydroxides. The flame-retardant properties of nanocomposites based on polypropylene (PP), polyethylene (PE), and polystyrene (PS) polymers have all been studied and reported. In addition, nano-hydroxides and  $\alpha$ -ZrP have also been studied to some extent (Wi et al., 2015). The results of these studies show that the flame retardancy of a single polymer/nanocomposite material is not ideal, and it is difficult to pass some flame-retardant test tests, thus limiting its use to a large extent. There is a lack of organic intercalation agents or surface modifiers for the main purpose of improving the flame retardancy in the research process. Moreover, these organic modifiers are polymers, which are not only inflammable, but also have low thermal stability. It is easy to degrade at high temperature, and the ignition time will be shortened when burning. It is not suitable for engineering plastics with higher processing temperature.

The compatibility between the traditional intumescent flame retardant and the non-polar PP matrix is poor, the amount of addition is large, and easy to agglomerate. At the same time, the flame-retardant effect is improved and the mechanical properties of the material are sacrificed. In addition, Chen et al. pointed out that some flame-retardant components of the intumescent flame retardant are easily soluble in water and leakage affects the retention of the material's long-lasting flame retardancy (Chen et al., 2013). These disadvantages lead to low flame-retardant efficiency and limit the scope of use. In order to overcome these problems of mixed intumescent flame retardants, Wu et al. achieved better results using melamine-formaldehyde wrap APP (Wu et al., 2013). The advantages of this technology are that it can change the appearance of the flame retardant, enhance the compatibility between the flame retardant and the matrix, effectively reduce the water solubility of the flame retardant, and improve the thermal stability of the flame retardant. However, the disadvantages such as uneven wrapping and easy cracking still need to be optimized.

Polymer/nano-flame retardant composites are one of the most active areas in the field of nanocomposite materials. In the flame-retardant technology, the synergistic flame-retardant effect is increasingly applied. The nano flame retardant system and the intumescent flame-retardant system not only meet the requirements of environmental protection, but also have high flame-retardant efficiency. The research on the compounding and synergistic effect between nano-flame-retarding system and intumescent flame-retardant system has become a new method for the development of modern flame-retardant technology. In a large number of polymer/nano-flame-retarded composite technologies, the  $\alpha$ -zirconium phosphate nano-flame retardant technology is a rookie in the research of flame-retardant polymers/nanocomposites. It has a unique ability to catalytic carbon, which has attracted the attention of researchers. The flame-retardant effects of  $\alpha$ -ZrP and MMT in polyvinyl alcohol (PVA) were compared (Chen and Wolcott, 2015). The study found that the heat release rate of PVA/ $\alpha$ -ZrP was more pronounced than that of PVA/MMT. The  $\alpha$ -ZrP modified with methylamine as the modifier can be used as a synergistic flame retardant, which can effectively improve the flame-retardant effect of the intumescent flame-retardant coating. These findings indicate that the flame-retardant properties of the polymer composites are associated with the physical barrier effects of the zirconium phosphate zirconium nanoparticle sheets. The most important thing is that it has catalytic function as a solid acid itself. In combination with the traditional flame retardant, it can catalyze the formation of carbon and increase the barrier and heat transfer effect of the carbon layer.

To sum up, the above research work mainly focuses on the research of nano flame retardant and intumescent flame-retardant technology in polypropylene flame-retardant system. However, a single nano flame retardant has low flame-retardant efficiency and dosage. It is usually combined with other flame retardants to improve the flame-retardant efficiency. The intumescent flame-retardant system has the advantages of being halogen-

free and releasing less toxic and harmful gases when it is burned. The traditional intumescent flame retardant has the disadvantages of poor compatibility with the matrix and easy moisture absorption. Therefore, for the zirconium phosphonate, the flame-retardant properties of polypropylene/ZrO<sub>2</sub>/layered double hydroxides and the intumescent flame retardancy of polypropylene/ternary hybrid zirconium phosphonate were studied.

### 3. Methods

#### 3.1 Molecular design of phase change energy storage thermal infrared interference materials

PEG is an important phase change energy storage material. According to its different molecular weights (several hundred to hundreds of thousand) and its regular change in enthalpy of phase changes, the phase change energy storage materials can be prepared by using PEG with different molecular weights. However, the phase change of PEG belongs to solid-liquid phase change, so its application is relatively simple when it is used as phase change material.

##### 2.1.1 PU phase change energy storage materials

PU is soft-hard alternating heterochain polymer with repeated -NH-COO- characteristic groups. Its molecular structure formula is shown in Figure 2-1, which is produced by the polymerization reaction between polyol and polyisocyanate. The polyol is a soft segment, and the isocyanate and chain extender are hard segments. Figure 1 shows the structure of PU molecular chain.

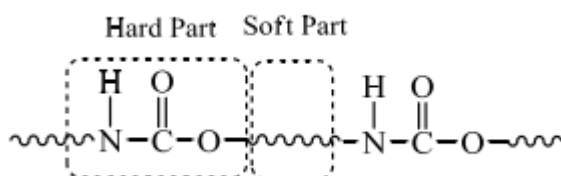


Figure 1: Structure of PU molecular chain

Polyurethane phase change material (PUPCM) is a kind of segmented copolymer composed of flexible segment with large molecular weight and rigid segment with relatively small molecular weight. The structure of PUPCM is similar to that of ordinary PU. Its hard segment is composed of chain extender and isocyanate to form a hard segment micro domain that serves as the backbone of PUPCM. The soft segment is composed of macromolecule polyol with phase change function, which is used as the function carrier of PUPCM. PUPCM is a kind of S-SPCM with large enthalpy of phase change, good thermal stability, adjustable phase change temperature and simple production process so that it has great development space and industrial prospect.

##### 2.1.2 Phase change energy storage thermal infrared interference composites

Infrared wave-absorbing material is a kind of special functional material with strong absorbing ability to one or several frequency bands in the infrared region. The special structure of nanometer material makes it have unique performance and advantages in the field of infrared wave absorption. However, macro bulk objects with the same texture as nanometer material don't have the characteristics of infrared wave absorption, shown in the following two aspects.

###### 1) Broad band strong absorption

The infrared absorption spectrum shows that with the decrease of particle size, the specific surface area of nanocrystal increases and the proportion of surface atoms increases. The difference between the interface atoms and the inner layer atoms leads to the widening of the infrared absorption peak.

###### 2) "Blue shift" phenomenon of nanoparticle

There are a large number of broken bonds on the surface of nanocrystal and the delocalized electrons are redistributed between the surface and the bulk phase, which increases the force constant in the region and the bond intensity, leading to the rise of the infrared absorption frequency and the blue shift of the infrared absorption peak. Nano-powders such as nano-Al<sub>2</sub>O<sub>3</sub>, nano-TiO<sub>2</sub> and nano-SiO<sub>2</sub> have strong absorption effect on the infrared waves of medium and far wave bands after being combined with polymer fiber.

#### 3.2 Dehydration pretreatment of raw materials

In preparing the raw materials for polyurethane infrared jamming phase change material (PUIJPCM), moisture may exist in PEG and NS and hydrone may react with -NCO group to produce unstable carbamic acid that

decomposes quickly to amine and release carbon dioxide. However, amine will react further with -NCO to produce substituted urea that may react further with -NCO to produce biuret. The reaction formulas of hydron and isocyanate are shown in Figure 2 and Figure 3.

These reactions will greatly consume -NCO groups, and the substituted urea and biuret produced by these reactions will rapidly increase the viscosity of the system and decrease the fluidity of the system. Carbon dioxide produced by these reactions will not escape from the system after the viscosity rises rapidly, which will easily cause a large amount of gas gel in the system so that the normal polymerization reaction cannot be continued. Therefore, before the reaction, PEG and NS must be conducted vacuum drying and dehydration to remove hydron as much as possible.

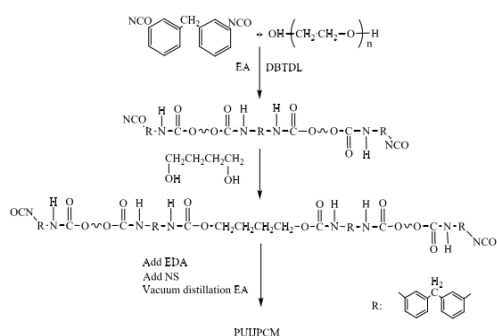


Figure 2: Preparation schematics of PUIJPCM

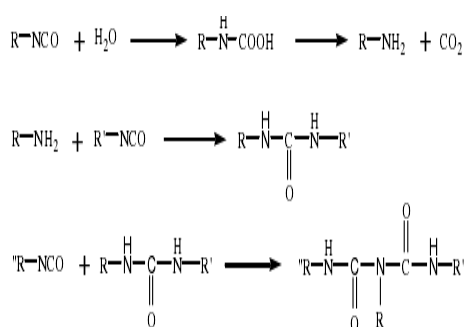


Figure 3: Reaction of isocyanate with water

### 3.3 Experimental procedures

The study uses PEG with different molecular weights as phase change unit, MDI as hard segment, DBTDL as catalyst, NS as dispersing agent, reinforcing agent and wave-absorbing material. With the help of chain extender (BDO) and neutralizer (TEA), a series of PUIJPCMs are prepared. The factors influencing the performance of PUIJPCM are analyzed in detail, including appearance test, storage stability test, thermal stability test, thermal decomposition test, infrared spectrum test, so as to determine the best formula so that the phase energy thermal infrared interference composites are with phase change temperature suitable for human wear, good thermal stability and certain wave-absorbing ability.

#### 2.3.1 Preparation of phase change energy storage thermal infrared interference materials

Figure 4 is preparation flow chart of PUIJPCM. In that reaction, EA which is less toxic than the traditional solvent, such as acetone and dimethylformamide for preparing PUPCM, is used as the solvent. EA is recycled to avoid environmental pollution. NS is used to improve the infrared absorption characteristics of PUPCM to obtain PUIJPCM.

The correlation coefficient can basically reflect the relationship between the molecular weight of PEG and its enthalpy of phase change. The enthalpy of phase change of PEG increases rapidly when the its molecular weight increases while its increase rate decreases, and then starts to decrease slowly after reaching the extreme value. As can be seen from Figures 2-5, when the molecular weight of PEG reaches 6,000, its enthalpy phase change is the largest. This may be because when the molecular weight of PEG is less than 6,000, the number of chain links of PEG macromolecules is less, the molecular chain is shorter, and the number of chains as end points is more. The content of chain links that can participate in crystallization is lower, and the crystal defects are more. These defects lead to a decrease in the crystallinity of PEG, thereby reducing its enthalpy of phase change. When the molecular weight of PEG is more than 6,000, the molecular chain of PEG is so long that PEG macromolecules are liable to intertwining with each other, which will also hinder the formation of regular crystals, leading to the decrease of the crystallinity of PEG and the decrease of its enthalpy of phase change. Tanking shell temperature (36.5 °C) and formulas 2-1 and 2-2 into consideration, this study proposes to use PEG2000 as the soft segment material of PUIJPCM.

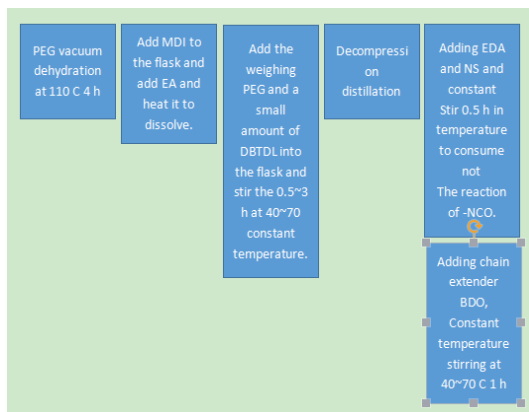


Figure 4: Preparation flow chart of PUIJPCM

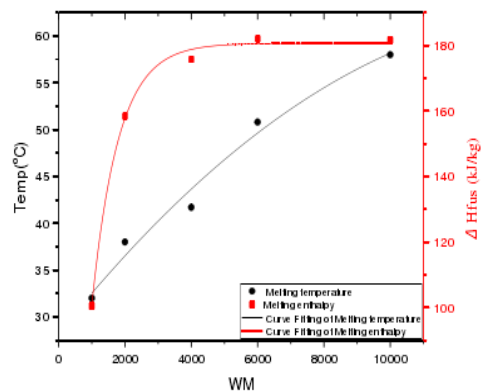


Figure 5: Melting temperature and melting enthalpy of PEG with different molecular weights

### 2.3.2 Orthogonal design

Referring to the previous literature, this study takes R values as 4, 6 and 8 respectively. The dosage of NS is set at 6%, 8% and 10% of total solids. R value, reaction temperature, reaction time and dosage of NS are taken as influence factors, and particle size distribution of PUIJPCM is used as evaluation index to evaluate each formula. The orthogonal experimental design is shown in Table 1.

Table 1: Factors and levels of orthogonal experimental design

Factor / level	NS	R value	reaction temperature	reaction time
1	6	4	40	60
2	8	6	50	120
3	10	8	60	180

## 4. Results and Analysis

### 4.1 Results of orthogonal design

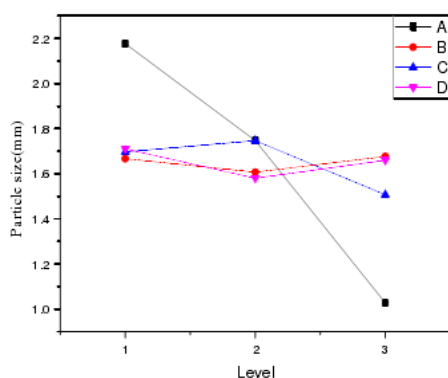


Figure 6: Effect of the orthogonal experiment factors on the M-WPUPCM emulsion particle size

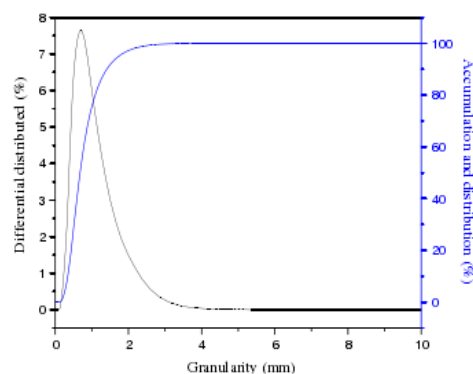


Figure 7: Test chart of PUIJPCM particle diameter

According to the orthogonal experimental result of PUIJPCM and the size of the range, it can be judged that the fluctuation size of the data of each factor is A (NSwt%) > C (reaction temperature °C) > D (reaction time

min) > B (R value). And the size of deviation reflects the dispersion degree of each factor:  $A > C > D > B$ , that is, the order of influence of each factor is  $A > C > D > B$ . In terms of the size of the experimental results, the content of NS and reaction temperature should be considered first and then the reaction time and R value should be considered in selecting the optimal process.

As shown in Figure 6, the particle size of factor A is the smallest at level 3, so the optimal plan is A3B2C3D2, that is, in the optimal experimental plan, NS is 10%, R value is 6, reaction temperature is 60 °C and reaction time is 120 min. Since the combination of this plan does not appear in the existing orthogonal design table, it needs to be re-prepared.

The PUIJPCM prepared based on plan A3B2C3D2 has an average particle diameter of 0.81 mm after the particle diameter test, as shown in Figure 7. The result is consistent with the result of orthogonal design, so it can be used as the optimal plan for the preparation of PUIJPCM.

#### 4.2 Test result of flame resistance

According to the flame resistance standard GB/T 5454-1997 "Oxygen Index Method of Textile Combustion Performance Test", the LOI value of flame resistance fiber needs to be more than 27% to be called flame resistance fiber. The limit oxygen index is conducted for testing VF and FRVF. The LOI test results show that only when the LOI value of FRVF-1 is more than 27% can it be called flame resistance fiber. Although FRVF-2 and FRVF-3's flame resistance performance is improved, they can't be called flame resistance fiber. Adding CGCP into viscose fiber can effectively increase the LOI value of the fiber, indicating that CGCP is a flame resistance material suitable for viscose fiber.

### 5. Conclusions

This study aims at understanding the energy storage and flame resistance of architectural organic composites. Firstly, it carries out molecular design of phase change energy storage thermal infrared interference materials. In this process, PU phase change energy storage materials and phase change energy storage thermal infrared interference composites are mainly designed. Then the dehydration pretreatment of the raw materials is conducted to complete the preparation of the experimental materials. In order to ensure the correctness of the experimental materials, the corresponding experimental procedures are carried out. The experimental procedures are mainly divided into two parts: the preparation of phase change energy storage thermal infrared interference materials and the orthogonal design. From the two parts, it is confirmed that the study is correct. The results of orthogonal design and flame resistance tests show that CGCP is an effective energy storage and flame resistance material. It is also found that the flame resistance of the architectural organic composite CGCP is more remarkable after adding the flame retardant of viscose fiber. The results show that this study can verify the application value of the architectural organic composite CGCP.

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