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**The flame retardant, mechanical properties and thermal conductivity of
polymer nanocomposites**

A Thesis Presented

by

Jie Li

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in Partial Fulfillment of the

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Abstract

Nanoparticles are great additives to the flame retardant and thermal properties of the polymers, however, they generally have some disadvantages on the mechanical properties. The mixing of polymers and nano-fillers such as Cloisite clays, melamine polyphosphate, molybdenum disulfide and graphene are mostly physical reactions between them and do not have chemical reactions during blending. And well dispersion is necessary to increase the conductive pathways, meanwhile, to reduce the loss of mechanical properties. Some of them are used for enhancing the self-extinguishment of PLA, which can form charring layer covered on the surface of samples to hinder the burning process. Generally, the better the nano-fillers disperse in the polymer matrix, the easier the material will intumesce and form charring layer during combustion, and on the other hand, the lower loss of mechanical properties the

composite has. Besides, graphene is always applied to improve the thermal conductivity of polymers because of its excellent thermal conductivity. And the mechanism of how to enhance this physical property has been discovered in the whole research. In this study, we focused on the most popular polymers like polypropylene (PP), polystyrene (PS), polylactic acid (PLA) and poly (methyl methacrylate) (PMMA). And the nanoparticles we used are Cloisite clays, melamine polyphosphate (MPP), molybdenum disulfide (MoS_2), graphene (GNPs), Ce-RDP and C-RDP. The last two particles were general additives cellulose and Cloisite clay sodium coated by RDP, respectively. We successfully obtained some blending materials which have excellent flame retardancy, however, the mechanical properties like impact and tensile had reduced more or less tested by Izod impact tests and tensile testing. In this paper, we also determined that graphene played an important role in improving the thermal conductivity of PP, PS and their immiscible blending with other polymers. And there were many factors like the degree of crystallinity of polymer matrices, the similarity of polarization between graphene and polymers, the mixing time and temperature, affect the rate of thermal conductivity enhancement to some extent.

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List of Abbreviations

C-Na⁺: Closites sodium

C-20A: Closites 20A

C-30B: Closites 30B

RDP: Resorcinol di (phenyl phosphate)

C-RDP: Mixing of Closites sodium and RDP

Ce-RDP: Mixing of Cellulose and RDP

MoS₂: Molybdenum disulfide

GNPs: Graphene

MPP: Melamine polyphosphate

MMT: Montmorillonite clays

PP: Polypropylene

PS: Polystyrene

PLA: Poly (lactic acid)

PMMA: Poly (methyl methacrylate)

SEM: Scanning electron microscope

TEM: Transmission electron microscope

T_g: Glass transition temperature

T_m: Melt temperature

NG: None grade

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Chapter 1. Introduction

In recent years, the traditional materials such as metals and ceramics cannot satisfy the large demands for functional materials and have been replaced by polymer and its composites step by step. Hence, the field of polymers has attracted strong attentions to improve physical and chemical properties and create special functional properties for newly developing fields. According to the advantages of light weight, easily formation in shape and low cost, Polypropylene (PP), Polystyrene (PS), Poly (methyl methacrylate) (PMMA) and Poly (lactic acid) (PLA) are extensive used in a wide range of fields and applications such as coatings, electronic productions, textile industry, medical instruments and biological materials. In addition, these polymers are located in the list of recycling plastics because of their less production of potentially harmful by-products or released additives. In the Society of Plastic Industry (SPI) plastic identification code, #5 is for PP, #6 is for PS, and PMMA and PLA are both contained in the group 7 because PMMA does not produce harmful bisphenol-A subunits and PLA is a biodegradable and biocompatibility polymer [1].

Always, blending of two polymers has been considered as an economical and also easily to combine the physical and mechanical properties of components or sometimes bring novel functional properties that individual polymer does not possess [2]. Besides, polymer blends are currently receiving great attention because they offer low-cost alternatives to the development of entirely new materials with improved properties [3]. This kind of blends can be defined as the mixture which has no covalent bonds between components [4]. It should be noted that in the polymer blends the properties of the final product is not only depending on

the intrinsic properties of both phases and the concentrations of various components in different phases but also related to their compatibility and morphology, even the adding sequence, time and temperature during blending [5-6]. As a result of thermalplastic properties, these four polymer and their blends are easy to make samples by molding with the process of compounding and hot pressing. In other words, we can mix them together or with additives when the producing temperature is above a special point like glass transition temperature (T_g) or melting temperature (T_m), and then obtain molding samples with various sizes according to different tests needed. After blending, the morphology of polymer blends depends on the concentrations of both polymer matrices, also the compatibility and miscibility of polymers. PP has nonpolar molecular chains according to its order molecular structure which has an average distribution of electron atmosphere shown in Figure 1. On the other hand, the polymer chains of PS, PLA, and PMMA contain polar functional groups shown in Figure 2, Figure 3 and Figure 4 respectively, which cause the weak polarization of PS and the strong ones of PMMA and PLA. Hence, the blends PP/PLA, PP/PMMA and PS/PMMA are immiscible blends because of the difference of molecular polarization. Actually, only a few polymer couples are completely or partially miscible and most of them are completely immiscible [7]. And the morphology is generally shown in two types in Figure 5: (a) sea-island phase dispersed into continuous phase or (b) a cocontinuous structure observed by electron telescopes, depending on the concentrations of each component.

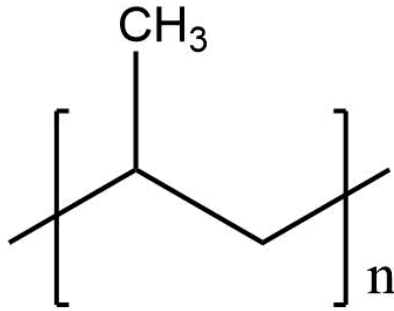


Figure 1. The structure of PP

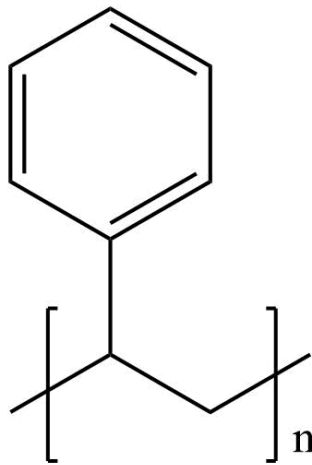


Figure 2. The structure of PS

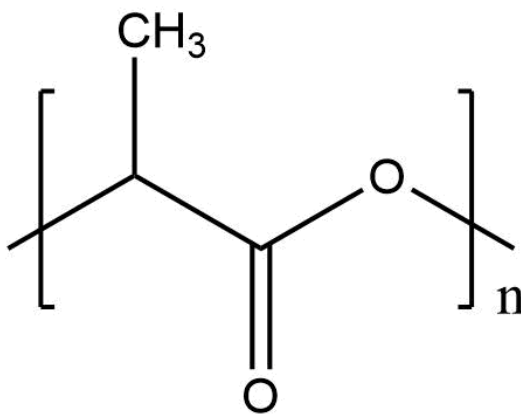


Figure 3. The structure of PLA

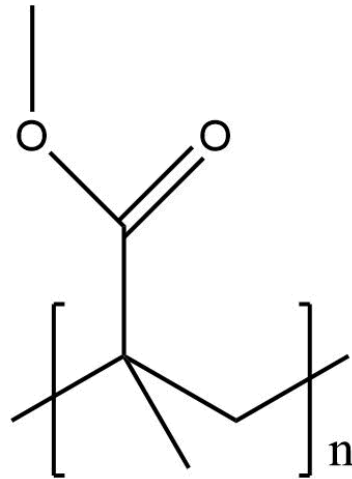


Figure 4. The structure of PMMA

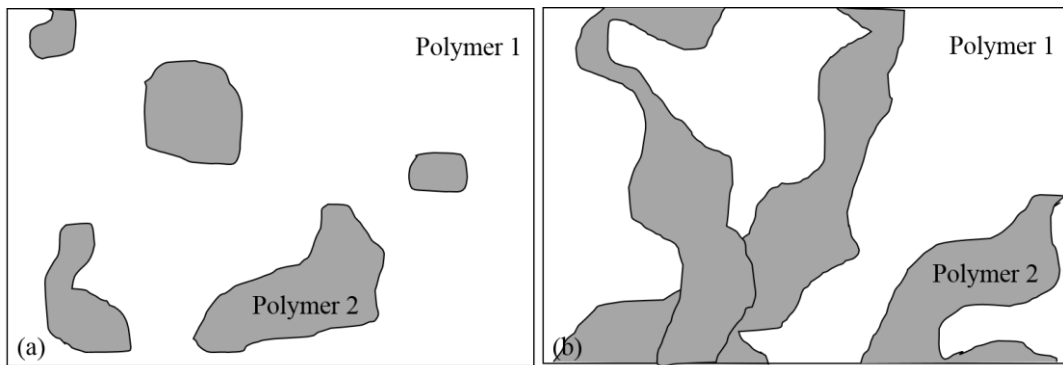


Figure 5. The graphic structure of immiscible polymer blends: (a) sea-island like structure; (b) cocontinuous structure

Because of the phase separation inside the polymer blends, the effect of interfaces and interphase interactions are not ignored during production processing. In general, the interface is normally applied to systems involving two or more condensed phases, while the concept of the surface is applied to the region between different physical forms like condensed (solid or liquid) phase and a gas phase or vacuum environment [8]. Hence, the term “interface” is better to interpret the boundary between immiscible polymer components. In addition, the properties of the polymer blend will be changed greatly from one phase to another. And the

thermodynamic energy is affected by the present of interfaces yet, i.e. the energetic situation is altered with the change of surroundings and/or components. The main limitation is that nanoparticles only work in the condensed phase (the solid or melt polymer itself) and do nothing to hinder the flame in vapor phase [13]. When polymer blending is modified by adding nanocomposites as graphene and clay, the additives will selectively locate at one phase or on the interface between polymer matrices, which depends on the polarization and crystallinity of both polymer matrices and nano-scale additives. In this paper, PP is a crystalline and nonpolar matrix, PS is amorphous and weakly polar, PMMA is amorphous and strongly polar, and PLA is crystalline and polar. When we add additive during the mixing process, the nanoparticles will move and locate according to the thermodynamic rules, which cause various morphologies shown by scanning electronic telescope (SEM) or transmission electronic telescope (TEM).

It has been proved that nanoparticles like organically modified montmorillonite (MMT) clays can effectively improve the thermal properties, modulus, and even flammability when mixed into the polymer [8-11]. C-20A and C-30B are used in common, which are modified C- Na^+ clay via the cation exchange with quaternary ammonium chloride salts, to increase the physical and mechanical properties. The structure of C-20A and C-30B are shown in Figure 6 and Figure 7 respectively. MMT is partial exfoliated on the interface of polymer matrices and the better exfoliated the clay is, the more strengthened the polymeric composite is. As the mixing of MMT clays and polymers is a single physical reaction, the dispersion of nanoparticles is related to the interface energy between polymers and clays as we discussion before. On the other hand, the higher toxicity of these two clays hinders the usage in several

fields. Besides, they will release toxic chemicals when the operating temperature is over a certain value. Hence, sometimes they cannot be used in flame retardant composites which need to suffer higher environmental temperature and have non-toxic released substances (both nanoparticles and gas) during burning and melting conditions.

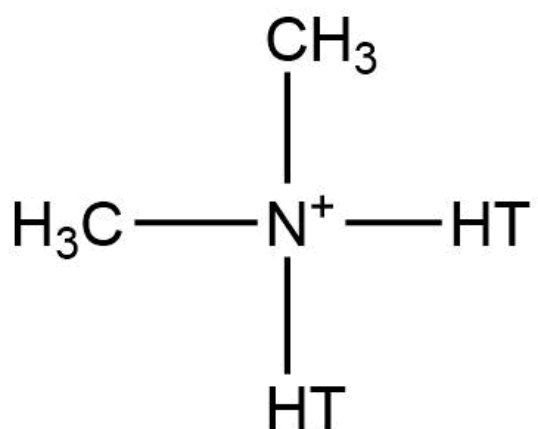


Figure 6. The structure of C-20A

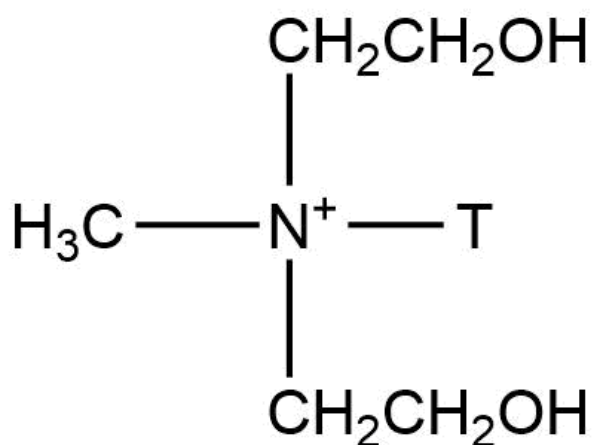


Figure 7. The structure of C-30B

With the development of synthetic and modified technology, some more environmental friendly additives were used as alternatives of these traditional clays and they can achieve the

improvement of the composites as well.

According to the Figure 8, the molecular structure of resorcinol di (phenyl phosphate) (RDP) can be coated on C-Na⁺ clays or cellulose and form C-RDP and Ce-RDP respectively, which is safer than ammonium chloride salts. From previous research, it can be proved that RDP absorbed clay achieves an advantage of large exfoliation in some kinds of polymer matrices like polystyrene [12]. In this paper, we do more further research to study the properties of C-RDP mixed with PLA. In addition, RDP coated cellulose is also served as a flame retardant added in PLA with the UL-94 test as follow, which will not release any toxic gas. Generally, RDP is a good flame retardant, however, as a liquid material, it decreases mechanical properties of polymeric composites. Hence, we need to reduce the amount of usage and the well-distributed coating is essential, which can obtain by centrifugal machine. The easy coating and well dispersion make it more effective to reduce the gas diffusion and thermal conductivity.

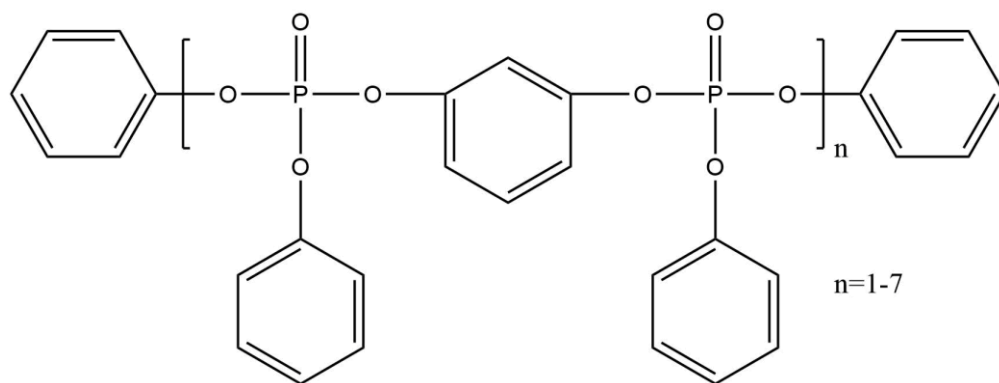


Figure 8. The structure of RDP

Graphene, a molecular sheet of graphite (3.35Å thickness in equal), has great potential applications in various fields for developing nanocomposites, sensors, hydrogen storage and thermally conductive materials. The special functions of graphene are related to one or more

fundamental properties such as excellent thermal, mechanical, electrical, transport, gas barrier and thermoelectric properties [14]. Graphene is easy to exfoliate than graphite because there is a strong cohesive between graphene layers in graphite. The thermal conductivity of graphene-based polymer nanocomposites is generally much lower than that of pure graphene because of the heat transfer process related to distribution and morphology of graphene located in the polymer matrix. The flammability is reduced because the excellent thermal conductivity of graphene, and when one side of the specimen is combusted, graphene can help conduct heat to another side so the temperature will not reach the ignition point, in order to retard flame. Jae-Yong Choi et al only add 0.09 wt% to achieve a large improvement of heat transport with encapsulating process [15]. The lower filler content of graphene can achieve well dispersion and bring the larger surface area to obtain effective thermal properties of polymeric composites. In general, the average mechanical properties of graphene-based materials is dropped by internal defects and this is still promising with some extent [16].

Apart from graphene, molybdenum disulfide (MoS_2) is one of the most important 2-D layered materials. The basic unit consists of a molybdenum atom coordinated with six sulfur atoms, shown in Figure 9. Because of the special sandwich structure, MoS_2 was introduced into PS to improve the fire resistance and thermal stability which compared that of the neat matrix [17]. The well distribution of layered additives may cause the barrier effect which can slow down the decomposition process and as transitional metal elements, Mo can form a charred layer during burning to protect materials from heat radiation and combustion-supporting gas [18]. K. Zhou et al documented that only low loading MoS_2 added can bring

much higher thermal stability and smoke suppression properties than that amount added of GNPs [19]. Therefore, we introduced MoS₂ into PLA and the samples were used for UL-94 test to characterize the increase of flame retardancy. Additionally, we mixed MoS₂ with MMT clays to decrease the toxicity of MMT and improve the thermal stability and fire resistance of polymer nanocomposites which reported in previous researches.

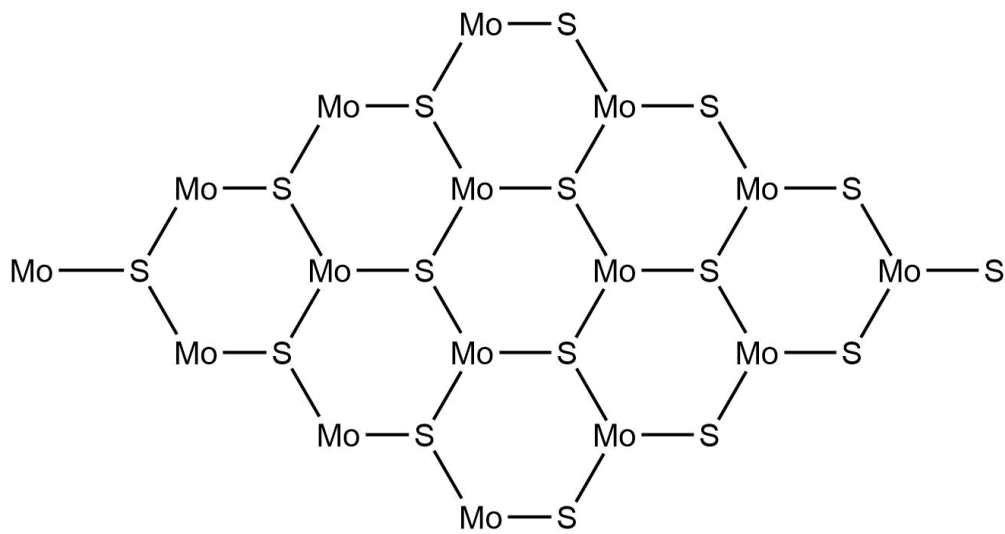


Figure 9. The structure of MoS₂

For the flame retardant additive, non-halogen and nontoxicity is essential. Melamine polyphosphate (MPP), the structure shown as Figure 10, is widely used as a flame retardant blending with several polymers. It is a good char-forming material and formed as intumescent flame retardant. The layer of char play an important role during combustion process to cut off heat transition and combustion-supporting gas. Thermal stability is affected greatly when MPP was introduced into polymer composites [20]. We also obtained this results from flame retardant test of PLA/Ce-RDP/MPP and PLA/MoS₂/MPP nanocomposites. Different mass ratios of components were mixed and compared by UL-94 test.

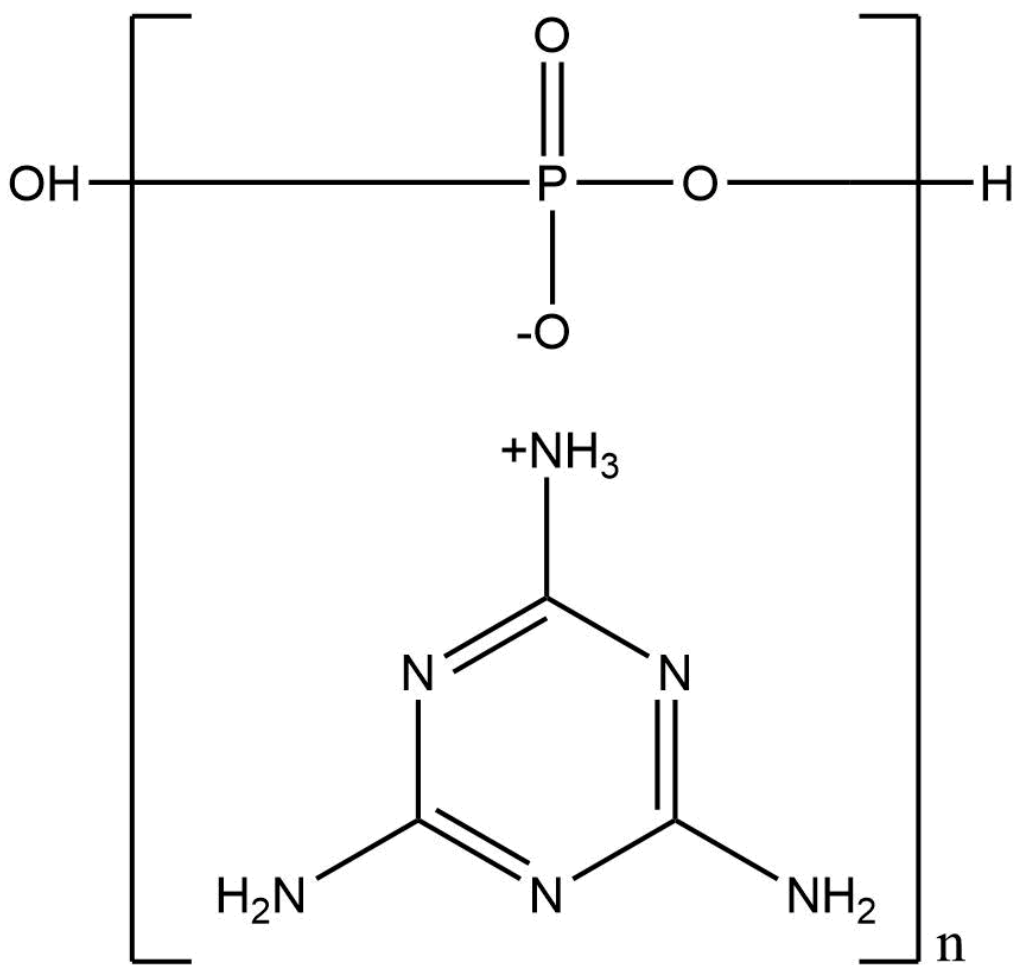


Figure 10. The structure of MPP

Chapter 2. Experimental Section

2.1 Materials

Poly (lactic acid), PLA 4020D, was purchased from the Natureworks LLC with a density of 1.24 g/cm³ and an average molecular weight of 120000 g/mol. Polypropylene, PP 3825, was purchased from Amco Polymers[®] with a density of 0.905 g/cm³. Poly (methyl methacrylate) with an average molecular weight of 120K, and polystyrene with an average molecular weight of 280K were purchased from Sigma-Aldrich.

There are two types of modified montmorillonite organoclays analyzed in this paper, Cloisite 20A (C-20A) and Cloisite 30B (C-30B), supplied by Southern Clay Inc. C-20A is a natural montmorillonite modified with N, N-dimethyl dehydrogenated tallow quaternary ammonium chloride, while C-30B is synthesized via ion exchange between Na⁺ of the C-Na⁺ and bis (2-hydroxyethyl) methyl hydrogenated tallow quaternary ammonium cation. Graphene H-5 was purchased from XG Sciences' xGNP[®] with a density of 2.2 g/cm³. Molybdenum Disulfide (MoS₂) was purchased from Sigma-Aldrich with a density of 5.06 g/cm³, whereas melamine polyphosphate (MPP) was purchased from Boc Sciences[®] with purity above 98%. The RDP, known as Fyrolflex RDP, was a type of phosphorus flame retardant agent (FR) supplied by ICL-IP Inc.

2.2 Preparation of RDP coated C-Na⁺ (C-RDP) and Cellulose (Ce-RDP)

To prepare C-RDP, 20wt% of RDP was placed in a 200ml baker and heated in a vacuum oven at 70 °C. Then 80 wt% of C-Na⁺ was added in batches and stirred manually with RDP

until no liquid remained inside the container. And then the mixture should be transferred into a plastic sample holder, which is used to insert into a Thinky Mixer for further mixing. The procedure was set at 700 rpm and 5min. After each mixing, the large aggregating parts should be crushed by mortar and then centrifuged again. This process should be continued more than 5 times until the mixture is formed as a uniform part in the holder. After that, the mixture should be taken out and transferred back into the 200 ml baker. Finally, the sample was placed in a vacuum oven at 70 °C for over 24 hours in order to remove the moisture and complete the RDP coating. The procedure for preparing Ce-RDP is as same as before, but the ratio of cellulose and RDP would change to 40 wt% of RDP and 60 wt% of cellulose.

2.3 Preparation of nanocomposites

The nanocomposites were prepared by the method of melting blend in the C. W. Brabender shown as Figure 11 (a). In order to prevent the decomposition of polymers during blending process, the operation temperature need set around or less than melting temperature. Since the difference of melting temperature for various polymers, the operation temperature was set at 160 °C for PLA and 180 °C for PP. However, the property of thermal stability need the polymer suffering high temperature, so the operation temperature for thermal conductivity samples was set at 200 °C. The initial rotor speed was 20 rpm. PLA and additives were first poured into the chamber for melting. After that, the speed of rotor was increasing at 100 rpm for 10min. Then some of the mixture pieces were directly molded by hot pressure into different shapes for flame and mechanical tests needed, shown in Figure 11 (b).

The ratios of the samples for the flame retardancy test are shown in Table 1, while the samples for thermal conductivity test are shown in Table 2 – Table 6.

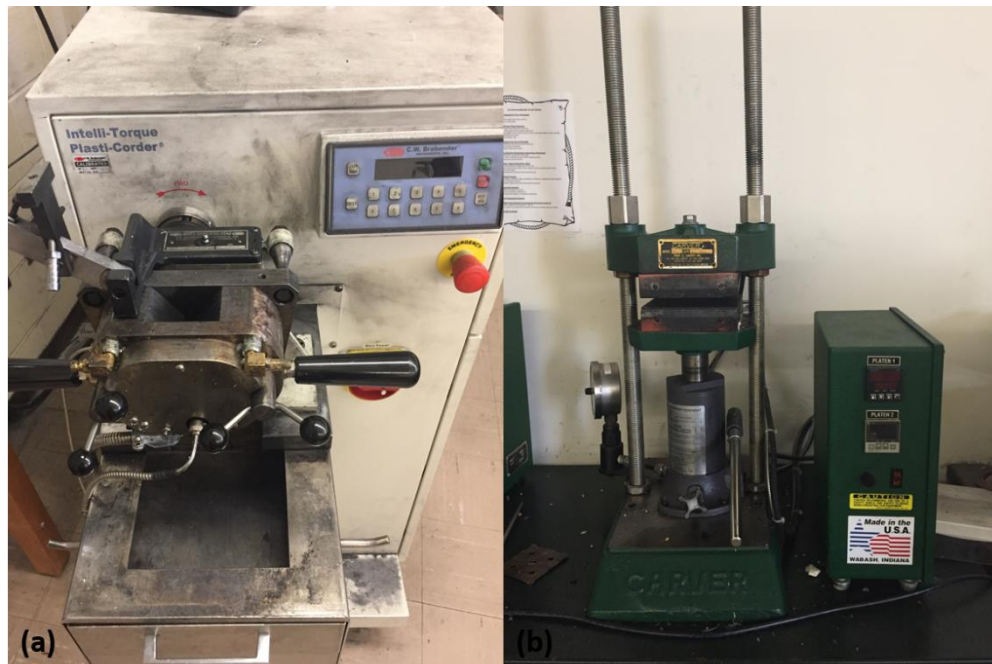


Figure 11. (a) Brabender; (b) Hot pressure

2.4 Characterization methods

2.4.1 Flame testing

UL-94 vertical burning test has been used to determine the ability of the samples to the self-extinguish and the extent of dripping. The results were analyzed related to the ASTM D 3801 standard. The dimensions of the specimens are 127 mm long, 12.7 mm wide and 3.2 mm thick. And we also put a piece of degreasing cotton under the combusting sample to test whether the dripping could combust the cotton or not, which is another important phenomenon to judge the flame retardancy of polymer nanocomposites.

2.4.2 Mechanical tests

Tensile properties of hot press molded were measuring with Instron 5542 provided by Instron Co. located in Grove City, PA, shown in Figure 12 (a). The extension rate set at 2.5 mm/min according to ASTM D-638, type M. The length for testing is 38.785 mm without bubbles containing the sample. And we use the first ten points from data to plot, and Young's modulus is the double time of average gradient. The tensile strength is the largest stress tested during the whole process and the elongation is the ratio of extension and the initial length of the specimen.

The impact strength of molded samples was tested by Izod impact tests which were conducted based on ASTM D-256, which specifies the dimensions of the samples were $63.5 \times 12.7 \times 3.2$ mm. The impact machine is shown in Figure 12 (b).

The results for each sample represented the average value of 5 specimens.

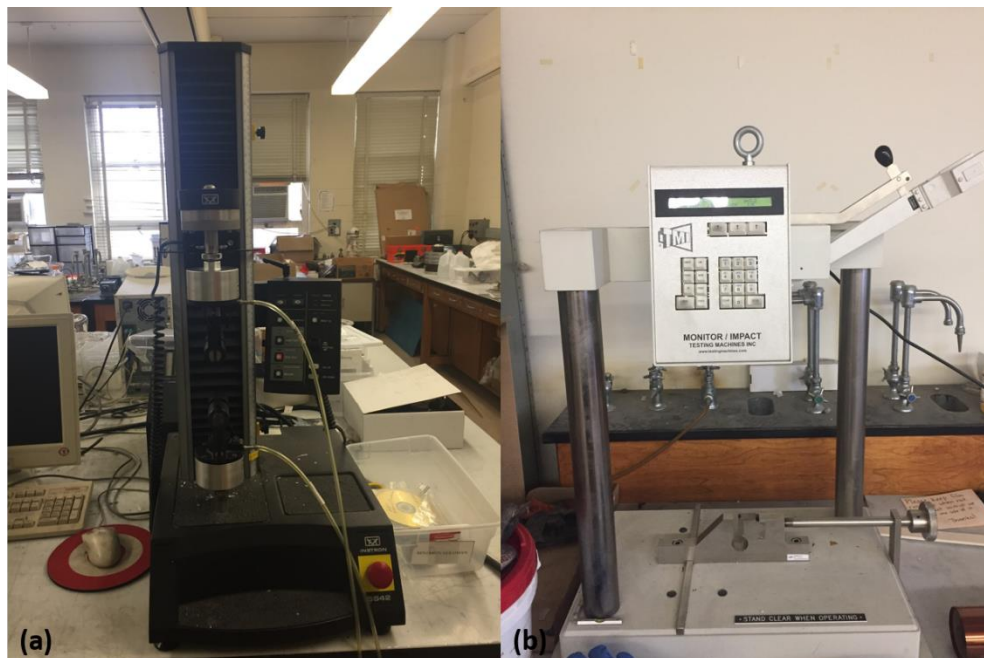


Figure 12. (a) Tensile test machine; (b) Izod impact test machine

2.4.3 Thermal conductivity testing

The thermal conductivity of molded samples was tested by Unitherm™ Model 2022 Thermal Conductivity Instrument, which shown in Figure 13. The thickness is 4 mm in common and if the thickness of sample has a tiny deviation, a correction has been used for the final result. The surrounding temperature during test process is pointed at 25 °C.



Figure 13. Utherm model 2022 thermal conductivity instrument

Table 1. Concentrations of nanoparticles used for PLA flame retardant test

Sample code	PLA (%)	Ce-RDP (%)	C-RDP (%)	C-20A (%)	C-30B (%)	MPP (%)	MoS ₂ (%)
PCeRDP1	90	10	-	-	-	-	-
PCeRDP2	88	12	-	-	-	-	-
PCeRDP3	85	15	-	-	-	-	-
PCeRDPC20A	87	12	-	1	-	-	-
PCeRDPC30B1	87	12.5	-	0.5	-	-	-
PCeRDPC30B2	87	12	-	1	-	-	-
PCeRDPC30B3	86	13	-	1	-	-	-
PCeRDPMPP1	83	12	-	-	-	5	-
PCeRDPMPP2	83	5	-	-	-	12	-
PCeRDPMPP3	80	10	-	-	-	10	-
PCeRDPMPP4	80	5	-	-	-	15	-
PMPPC20A	85	-	-	2	-	13	-
PMPPCeRDPC20A1	83	1	-	1	-	15	-
PMPPCeRDPC20A2	84	3	-	1	-	12	-
PMoS ₂ 1	90	-	-	-	-	-	10
PMoS ₂ 2	88	-	-	-	-	-	12
PMoS ₂ 3	85	-	-	-	-	-	15
PMoS ₂ CeRDP1	85	14	-	-	-	-	1
PMoS ₂ CeRDP2	85	13	-	-	-	-	2
PMoS ₂ CeRDP3	90	2	-	-	-	-	8
PMoS ₂ CRDP1	90	-	1	-	-	-	9
PMoS ₂ CRDP2	90	-	2	-	-	-	8
PMoS ₂ CRDP3	90	-	5	-	-	-	5
PMoS ₂ C20A1	90	-	-	1	-	-	9
PMoS ₂ C20A2	90	-	-	2	-	-	8
PMoS ₂ C30B	90	-	-	1	-	-	9
PMoS ₂ MPP1	90	-	-	-	-	2	8
PMoS ₂ MPP2	88	-	-	-	-	4	8
PMoS ₂ CRDPC20A	85	-	12	1	-	-	2
PMoS ₂ CRDPC30B	85	-	12	-	1	-	2
PMoS ₂ CRDPMPP	86	-	2	-	-	2	10

Table 2. Concentrations of nanocomposites used for PP thermal conductivity test

Sample code	PP (%)	PS (%)	PMMA (%)	PLA (%)	GNPs (%)
PGNPs0	100	-	-	-	-
PGNPs1	92.5	-	-	-	7.5
PGNPs2	86.5	-	-	-	13.5
PGNPs3	80	-	-	-	20

Table 3. Concentrations of nanocomposites used for PS thermal conductivity test

Sample code	PP (%)	PS (%)	PMMA (%)	PLA (%)	GNPs (%)
PGNPs0	-	100	-	-	-
PGNPs1	-	95	-	-	5
PGNPs2	-	90	-	-	10
PGNPs3	-	85	-	-	15
PGNPs4	-	80	-	-	20

Table 4. Concentrations of nanocomposites used for PP/PMMA thermal conductivity test

Sample code	PP (%)	PS (%)	PMMA (%)	PLA (%)	GNPs (%)
P1P2GNPs0	70	-	30	-	-
P1P2GNPs1	70	-	30	-	5
P1P2GNPs2	70	-	30	-	10
P1P2GNPs3	70	-	30	-	15
P1P2GNPs4	56	-	24	-	20

Table 5. Concentrations of nanocomposites used for PP/PLA thermal conductivity test

Sample code	PP (%)	PS (%)	PMMA (%)	PLA (%)	GNPs (%)
P1P2GNPs0	60	-	-	40	-
P1P2GNPs1	57	-	-	38	5
P1P2GNPs2	54	-	-	36	10
P1P2GNPs3	51	-	-	34	15
P1P2GNPs4	48	-	-	32	20

Table 6. Concentrations of nanocomposites used for PS/PMMA thermal conductivity test

Sample code	PP (%)	PS (%)	PMMA (%)	PLA (%)	GNPs (%)
P1P2GNPs0	-	60	40	-	-
P1P2GNPs1	-	58.8	39.2	-	2
P1P2GNPs2	-	57.6	38.4	-	4
P1P2GNPs3	-	57	38	-	5
P1P2GNPs4	-	56.4	37.6	-	6
P1P2GNPs5	-	55.2	36.8	-	8
P1P2GNPs6	-	54	36	-	10
P1P2GNPs7	-	51	34	-	15
P1P2GNPs8	-	48	32	-	20

Chapter 3. Results and discussions

3.1 Results and discussion of PLA/nanoparticles flame retardant tests

The main purpose of this project is to find some additives which are benefit for flame retardant of PLA and the optimal concentration of various additives which could reduce the damage of mechanical properties meanwhile improve flame retardancy of PLA. PLA is a flammable polymer which has been used widely in recent years. However, the poor flame retardant and heavy dripping phenomenon sometimes restrict its application. Therefore, to find a feasible approach to improve the flame retardant of PLA is the current purpose to be realized. Adding additives is an easier and cheaper method to compromise the need for special properties and traditional mechanical properties, compared with synthesizing a new functional polymer. The former research of PLA/organoclays found that only adding 5 wt% modified MMT can increase the Limit Oxygen Index (LOI) from 20.2% to 46% and the UL-94 reaches V-0 level, improving the flame retardant of PLA dramatically [21]. On the other hand, replacing a little part of traditional flame retardant, aluminum trihydrate ($\text{Al}(\text{OH})_3$), the hardness of PLA nanocomposites could improve to some extent. P. Kiliaris et al found that the more the concentration of carbon nanotube (CNTs) added, the less increase the heat release rate is and the more formation of charring produces [22]. Yichen Guo et al documented that only 1 wt% C-30B added into PLA/MPP nanocomposites could achieve self-extinguish by intumescent forming on the surface of the sample [9].

In this study, we tried to mix different kinds of IFR and blend with PLA, in order to find the optimum concentration which has better compromising between flammability and

mechanical properties such as impact and tensile properties. From former research, as an acid source and a blowing agent, melamine polyphosphate (MPP) is added less than 20 percent to hinder combustion property effectively. Moreover, MPP can help maintain mechanical properties at the same time, while for some other nanoparticles like MMT are not good for the physical mechanical properties of polymer matrix. Hence, we tried to add MPP with the novel coated particles, Ce-RDP, to reach the purpose of property improvement. Besides, we also had a systemic research of Molybdenum Disulfide (MoS_2), as a flame retardant acting on PLA. However, the large amount of MoS_2 added gave rise to a brittle and loose structure, which impeded molding and production during the test. According to UL-94 vertical combustion tests, V_0 means burning stops within 10 seconds on a vertical specimen and drips are allowed as long as they are not inflamed the cotton under the specimen. In other words, the sample is self-extinguish quickly and cannot ignite other things during all the time. However, most of the drips can ignite the cotton because when dripping is occurring, the drips always have a high temperature and covered by the fire. Therefore, we tried to mix organoclays or Ce-RDP with PLA/MPP system to keep the specimen from dripping during the combusting process. Cellulose is a biodegradable polymer which can degrade in the combustion and a large amount of heat will release. When dripping occurs, most of the released heat will disperse into the environment or was brought with drips. On the other hand, the released heat can help the degradation of cellulose, which can produce pyrolysis to mix with oxygen, so that combustion will be improved by the surrounding fire, causing a longer time to extinguish. That is why the cellulose is not performed well as MPP, however, when mixed with RDP, the result is better

than before. RDP is liquid alone and it will create more drips during combustion, as well as another additive MoS₂. As mentioned before, the drips can take away a large part of released heat from the specimen, so Ce-RDP is another method to help improve the flame retardancy of PLA compared with forming charring on the surface of the specimen. And we also added organoclays with MoS₂ to reduce the dripping phenomenon and the loss of physical mechanical properties. The results of UL-94 tests are listed in Table 7.

Table 7. UL-94 tests of PLA nanocomposites

Sample code	t ₁ (s)	t ₂ (s)	Dripping	Cotton combustion	UL-94 grade
PCeRDP1	1	2	Y	N	V ₀
PCeRDP2	2	1	Y	Y	V ₂
PCeRDP3	>30	-	Y	N	NG
PCeRDPC20A	11	2	Y	Y	V ₂
PCeRDPC30B1	6	12	Y	Y	V ₂
PCeRDPC30B2	16	-	Y	Y	NG
PCeRDPC30B3	19	-	Y	Y	V ₃
PCeRDPMPP1	0	10	N	N	V ₀
PCeRDPMPP2	0	10	N	N	V ₀
PCeRDPMPP3	2	10	N	N	V ₀
PCeRDPMPP4	1	1	N	N	V ₀
PMPPC20A	>30	-	N	N	NG
PMPPCeRDPC20A1	2	2	N	N	V ₀
PMPPCeRDPC20A2	3	3	Y	Y	V ₂
PMoS ₂ 1	2	2	Y	Y	V ₂
PMoS ₂ 2	0	0	Y	N	V ₀
PMoS ₂ 3	1	3	Y	Y	V ₂
PMoS ₂ CeRDP1	17	3	Y	Y	V ₂
PMoS ₂ CeRDP2	5	1	Y	Y	V ₂
PMoS ₂ CeRDP3	1	2	Y	Y	V ₂
PMoS ₂ CRDP1	1	4	Y	Y	V ₂
PMoS ₂ CRDP2	5	3	Y	Y	V ₂
PMoS ₂ CRDP3	5	5	Y	Y	V ₂
PMoS ₂ C20A1	3	>30	Y	Y	NG
PMoS ₂ C20A2	>30	-	Y	Y	NG
PMoS ₂ C30B	3	1	Y	Y	V ₂
PMoS ₂ MPP1	4	8	Y	Y	V ₂
PMoS ₂ MPP2	8	10	Y	Y	V ₂
PMoS ₂ CRDPC20A	7	19	Y	Y	V ₂
PMoS ₂ CRDPC30B	5	19	Y	Y	V ₂
PMoS ₂ CRDPMPP	10	-	Y	Y	NG

3.1.1 UL-94 vertical burning tests

According to Table 7, results of UL-94 tests showed that if Ce-RDP alone is added into PLA, 10 percent is the maximum amount to keep V₀ grade, which had drips but it was not combusting the cotton. When the percentage of Ce-RDP had a little increase to 12 percent, the self-extinguishing time is close to the former one, however, the drips could ignite the cotton until the cotton was burned out. Increasing the amount of Ce-RDP to 15 percent, the value of burning stop time t_1 is over 30 second and could not extinguish, while the cotton was not ignited because there was no dripping during the combusting process. The test of adding 15 percent Ce-RDP was fail and labeled NG, although the dripping phenomenon was disappeared successfully. Therefore, if we can find another additive which can help hinder dripping, meanwhile, reduce the time span of self-extinguishing. Therefore, Ce-RDP system is a considerable IFR because of the degradation property of both cellulose and RDP, i.e. they can easily degrade under the burning temperature. It makes the PLA/Ce-RDP mixture more likely to drop when carrying on UL-94 testing. On the other hand, drips of polymer composites can take away a large part of released heat and help specimen extinguish quickly, which yield the occurrence of dripping in return to some extent. However, as RDP is a liquid and cellulose is easy to degrade, the specimen will keep dripping with the increasing amount of addition. And the dripping so fast will make the cotton combustion before the fire covered on the drips extinguish by itself.

We tried to mix C-20A or C-30B with PLA/Ce-RDP system in various concentration, in order to find the minimum value of organoclay added. This is because nanoparticles could

cause structure defects inside the polymer matrices during blending and molding process, which might affect the mechanical properties of polymer blending. When we added only 1 percent C-20A or C-30B into PLA/Ce-RDP (87/12), the burning stop time increased to 11 second and 16 seconds, respectively. The UL-94 grade still maintained around V₂ level, even dropped to NG level. Another test was about PLA/Ce-RDP/C-30B (87/12.5/0.5), which had a better self-extinguishing time around 6 seconds but the cotton was still ignited by dripping. Some experiments were tried but not listed in Table 7 because the specimen could not be made with large amount additives and we could not have a combusting test directly. Meanwhile, another additive melamine polyphosphate (MPP) was used as an effective flame retardant, which documented decades ago, into PLA/Ce-RDP system. When we added only 5 wt% into PLA/Ce-RDP system, the burning specimen had extinguished immediately and no dripping occurred. The second ignition tested follow the first one and the sample extinguished in 10 second and drips was not dropped yet. That is not to say only 5 percent of MPP added into PLA can help improve flame retardant, a great advance when compared to those addition agents which more than 10 percent need to blend with PLA to pass V₀ grade. From 10 percent to 15 percent of MPP added, the UL-94 tests of these specimens had passed V₀ level and there were no drips appeared during the whole combusting process, so the cotton under the specimen was entire and not change after the vertical burning test. The better formula of PLA/Ce-RDP/MPP was 80/5/15 (listed as weight ratio), which displayed that the first self-extinguish time t₁ and the second one t₂ were 1 second and 1 second respectively, meanwhile, there was no dripping to ignite cotton during the burning process. Therefore, MPP played an important role on self-

extinguishing in order to hinder dripping phenomenon. Therefore, we tried to mix MPP with Ce-RDP/C-20A agent to analyze the dripping process. When we only added MPP and C-20A into PLA, the specimen was burned out and no dripping dropped during the burning process. With 1 percent of Ce-RDP and 1 percent of C-20A mixed, the PLA/MPP system passed V₀ grade of UL-94, which had no drips and extinguished in only 2 seconds. But when the concentration of Ce-RDP increased to 3 wt%, the value of t₁ only had a little increase, but dripping was occurred immediately and ignited the cotton until the cotton was burned out, which only passed V₂. This phenomenon directly proved that Ce-RDP could improve the dripping phenomenon during burning process and modified MMT like C-20A could reduce this phenomenon when the amount of Ce-RDP was not very larger than this of C-20A.

Recently, we found more literature and discovered that Molybdenum Disulfide (MoS₂) can work effectively on polymer retardant. Yuhua Zhong et al documented that MoS₂ could effectively enhance the thermal stability of thermoplastic polyester-ether elastomer (TPEE) nanocomposites and got V₀ ranking with no melt droplets during the vertical burning test [18]. Keqing Zhou et al proved that only 3 wt% of layered nano-filler MoS₂ could improve the thermal stability, fire resistance and smoke suppression properties of the PS nanocomposites simultaneously by the good dispersion and physical barrier effects of MoS₂ [19]. When the amount of MoS₂ added into PLA increased to 15 percent, the V₀ ranking could be passed with extinguishing immediately and drips but not igniting the cotton. However, MoS₂ is a kind of amorphous mineral material, which has a liquid phase exfoliation at a higher temperature. Hence, the dripping of polymer mixture is severe with MoS₂ added.

Then the reduction of adding concentration and droplets of PLA/MoS₂ system is considered in further research. When we added Ce-RDP or C-RDP at low loading amount, the polymer nanocomposites still had drips which ignited the cotton. While high loading amount of Ce-RDP caused extinguishing time extending to above 10 second and dripping was more serious than low loading samples because Ce-RDP is also an advance factor of liquidation and dripping. The phenomenon of low loading C-20A or C-30B or MPP was similar with former tests shown in Table 7. And the further mixing of MoS₂, C-RDP, and MPP or organoclays were not as good as possible, which even turned back to the level NG of UL-94 test.

In a word, PLA/MPP/Ce-RDP is the better formula to improve flame retardancy and reduce droplets simultaneously. And to consider the outlay and mechanical properties, we molded impact and tensile specimens to test which formula was the best one in this project.

3.1.2 IZOD impact properties of PLA nanocomposites

Impact strength is the capability of the material to withstand a suddenly applied load and is expressed in terms of energy. Often measured with the Izod impact strength test or Charpy impact test, both of which measure the impact energy required to fracture a sample. And the unit of impact strength is generally Joule per meter (J/m). Impact tests are used to study the toughness of materials, which is a factor of its ability to absorb energy during plastic deformation. PLA is a crystalline polymer which always displays a brittle character and will break during Izod impact test. The detail results of PLA/nanoparticles composites are listed in Table 8.

Table 8. Impact strength of PLA nanocomposites

Sample code	Concentrations (wt %)	Impact strength (J/m)
PLA	100	25.642
PCeRDP1	90/10	10.401
PMoS ₂ 3	85/15	-
PCeRDPMPP1	83/12/5	18.176
PCeRDPMPP2	83/5/12	27.334
PCeRDPMPP3	80/10/10	28.127
PCeRDPMPP4	80/5/15	26.528
PMPPCeRDPC20A1	83/15/1/1	53.925

The impact strength of pure polylactic acid was 25.642 J/m from former research in another relative project. According to Table 7, it is obviously that when the adding amount of MPP was above 10 percent and below 20 percent, the impact strength increased more or less. This is because MPP has a more hydrophobic radical group, which can help MPP distribute well in the polymer matrix and do not aggregate on the interface of polymer blending. And it is harder for them to form crack size. In addition, internal stress plays a major role on the formation of local cracks. If the nanoparticle has a large draw ratio or higher concentration, the crack inside the polymer matrix is harder to form. From the following formula, we can see the relation between the critical stress and draw ratio.

$$\sigma_{\max} = \sigma \left(1 + 2 \frac{a}{b} \right)$$

where a and b are the length and width of the particles in the matrix, σ is the applied force or external stress and σ_{\max} is the critical stress to break the specimen at the crack tip. It is clearly that if the draw ratio (a/b) increases, the critical stress increases and the sample is harder to break under the same applied force. On the other hand, at lower concentration of additives, the crack will be smaller than a higher one. And the higher concentration generally displays a better

exfoliation, which results in a fewer number of non-exfoliated particles existing and the longer distance between the nanoparticles. Then, it is more difficult to crack. Hence, the mechanical properties of MPP added polymer composites will reduce less than those of other nanoparticles added mixture. For example, MoS₂ or Ce-RDP alone mixed with PLA caused a large decrease of impact strength, even could not be molding for test. When we tried to add the lower amount of MPP like 5 percent with 12 percent of Ce-RDP into PLA, the specimens were easier to mold than the one with 10 percent of Ce-RDP and the value of impact strength only had a few reduction to 18.176 J/m. Therefore, Ce-RDP and MoS₂ mixed with PLA embrittled PLA, only MPP helped to maintain the impact strength. The best result of these samples is PMPPCeRDPC20A1, which had 15 percent of MPP, 1 percent of Ce-RDP and 1 percent of C-20A, with above one-time increase of impact strength (53.925 J/m). Besides the addition of large amount of MPP, small part of Ce-RDP was to improve flame retardancy and C-20A added was to reduce the droplets caused by Ce-RDP and PLA itself.

3.1.3 Tensile properties of PLA nanocomposites

The tensile strengths, elongation and Young's modulus results of PLA/Ce-RDP/MPP are listed in Table 8. From the former research, we can find that pure PLA generally has tensile strength around 60 MPa and Young's modulus around 3.5 GPa. However, when we tried to mix PLA with nanoparticles, the tensile property dropped substantially.

Table 9. Tensile test of PLA nanocomposites

Sample code	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)
PLA	57.80	~6.00	3.50
PCeRDPMPP2	30.00	2.38	2.92
PCeRDPMPP3	31.82	2.52	3.13
PCeRDPMPP4	33.00	2.69	2.97
PMPPCeRDPC20A1	38.50	3.18	3.85

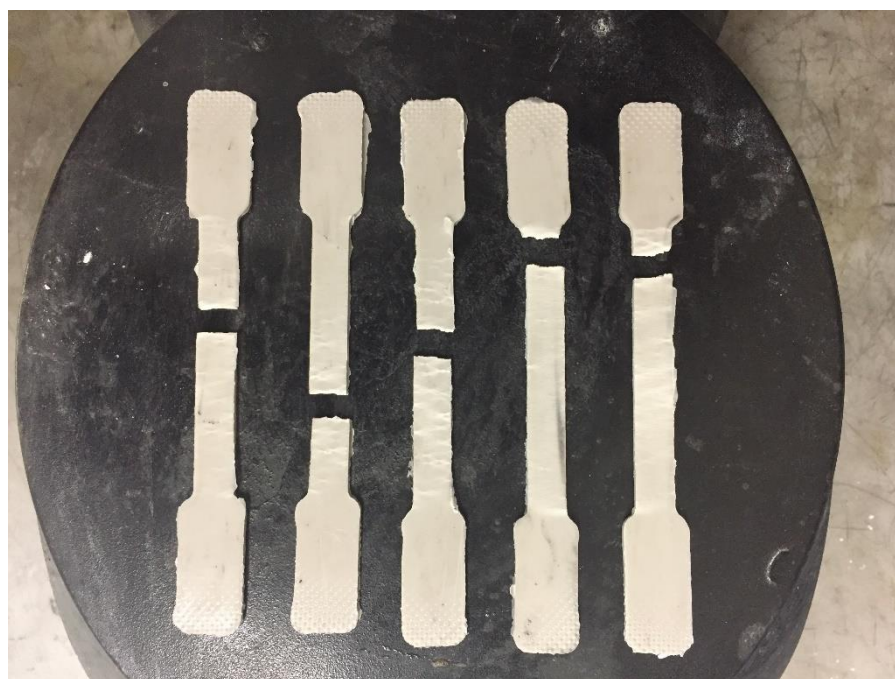


Figure 14. The specimens after tensile testing of 83PLA/15MPP/1Ce-RDP/1C-20A

We only test the samples with good flame retardancy, which means the V_0 grade passed during UL-94 test. But two of them, PLA/Ce-RDP (90/10) and PLA/Ce-RDP/MPP (83/12/5) could be molded because too many fillers added inside the polymer matrix, which brought internal defects and embrittled PLA. Another formula PLA/MoS₂ (85/15) also has better flame retardancy with heavily dripping phenomenon. And the samples made for mechanical tests was

very brittle and generally cracked during the cooling process.

With the decrease amount of Ce-RDP and relative increase amount of MPP, the reduction of tensile strength reduced but Young's modulus had less change around 3.0 GPa. The tensile strength of all samples was reduced around 50 percent, while the values of elongation was reduced over 60 percent. The reason is that nanoparticles added inside polymer matrix would aggregate together and easily form defects in nanocomposites, which resulted in local concentration of stress to crack sample. As mentioned before, MPP mixed with PLA/Ce-RDP system could help maintain the mechanical properties like impact and tensile ones. However, if the concentration of Ce-RDP was much higher, the effect of MPP would not as good as MPP alone added and the toughness of specimens would reduce dramatically with the increase of nanoparticles. The best formula in this project was PLA/MPP mixed with only one percent of both Ce-RDP and C-20A, respectively and the specimens after testing was shown in Figure 14. The value of tensile strength only decreased 33 percent than the pure one and the elongation reached to 3.18%, which the reduction was below 50 percent. On the other hand, Young's modulus improved to 3.85 GPa, which displayed the ability of large amount MPP mixed.

3.2 Results and discussion of GNPs H-5 polymer nanocomposites

In theoretically, thermal conductivity (always labeled as κ or λ) is a physical property of material to conduct heat at a certain environmental temperature. Heat transfer occurs at a lower rate across materials of low thermal conductivity than across materials of high thermal

conductivity. Sometimes, thermal conductivity of a material depends on temperature. Correspondingly, materials, which have higher thermal conductivity, are widely used in heat sink applications whereas the lower ones are applied as thermal insulators [27]. As mentioned before, graphene has the extraordinary thermal conductivity around $5300 \text{ W m}^{-1} \text{ K}^{-1}$ and extremely high surface area over $2630 \text{ m}^2/\text{g}$, which have made it the most promising candidate for fabrication of high performance thermal conductivity polymer composites (TCPCs) [23]. Unfortunately, the low loading of graphene mixed with polymer could not show high improvement of thermal conductivity, which still remains a challenge for recent years. In this project, we first made a series of polymer composites with various concentrations of graphene nanoplatelets (GNPs) H-5 and then molded for thermal conductive test to analyze the trend growth and which polymer or polymer blends the GNPs added had a larger improvement of thermal conductivity.

The increase of thermal conductivity is not only related to the mixing time and the concentration of graphene added inside the polymer but also is bound up with the polarization and the degree of crystallization of polymer matrices [23-28]. On one hand, graphene is a non-polar additive and has more possibility to locate at the phase with same or similar polarization, which means GNPs has special selective localization behavior during blending process [24]. In this paper, we used four different polymers as matrices, PP and PS are non-polar material or sometimes has weak polar because of the irregular structure, while PLA and PMMA have strong polar side groups caused stronger polar. Hence, GNPs generally locate in PP or PS phase or at the interface between two phases near PP or PS side when PP or PS blends with another

high polar polymer. However, during blending process, some part of GNPs located in the higher polar phase by the viscosity of melt polymer which resulted in the poor performance of thermal conductivity enhancement. Therefore, another method founded to trapped graphene located in only one phase to improve thermal conductivity. Jae-Yong Choi et al made a graphene-encapsulated PMMA composites to improve thermal conductivity dramatically than pure PMMA with only 0.9 wt% [15]. Cui Mao et al combined PS with PMMA, which takes charge of the strong polarization of PMMA to help PS absorb GNPs with relatively strong interaction between the graphene and the polymer chains, meanwhile, modify graphene coated with a non-polar material to enhance the non-polar property of graphene [26]. On the other hand, the crystallinity of polymer matrix will affect the absorption of GNPs inside the polymer blending. With the increased polymer chain alignment and crystallization, the thermal conductivity will improve in both experimental and computational works [27]. This is because graphene has a significantly different property between the in-plane and out-plane direction and the extreme thermal conductivity is obtained in the in-plane direction. The polymer with a high degree of crystallization has ordered molecular structure to maintain graphene located more regular than random distribution. However, Matthew C. George et al reported that this increase was not very significant in block polymer PS-b-PMMA [25]. And we tried to analyze the effect on immiscible polymer blending to prove the effect of crystallinity on thermal conductivity.

3.2.1 Thermal conductivity of PP nanocomposites

We first produced a series of polypropylene/graphene nanocomposites with different

concentrations of GNPs H-5. The thermal conductivity of PP/GNPs is listed in Table 10, in which the thermal conductivity is $0.223 \text{ W m}^{-1} \text{ K}^{-1}$ for pure PP system. As the loading of graphene increases to 20 percent, the result of PP/GNPs grew up to $0.678 \text{ W m}^{-1} \text{ K}^{-1}$, approximately 2 times increase of thermal conductivity.

Table 10. Thermal conductivity of PP/GNPs nanocomposites

Sample code	Concentrations (wt %)	Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)
PGNPs0	100/0	0.223
PGNPs1	92.5/7.5	0.372
PGNPs2	86.5/13.5	0.571
PGNPs3	80/20	0.678

From other research, it is noted that when the concentration of two polymers was 50/50 wt%, the cocontinuous formed would effectively help to trap graphene in similar polar phase. When the content of polar phase increased over 50 wt%, the thermal conductivity decreased by the loss of continuous interfaces and non-polar polymer phase which GNPs generally located inside [23]. Therefore, we selected 70/30 wt% of PP/PMMA system and 60/40 wt% of PP/PLA system to research the regular pattern of thermal conductivity. Both of these two systems had a lower thermal conductivity with no graphene added because of the immiscibility of polymer matrices. From Figure 15, we could find that the blending of both crystalline polymer PP/PLA had a higher thermal conductivity than the one with an amorphous and a crystalline polymer PP/PMMA without graphene added. When the low loading (<15 wt %) of graphene mixed with PP/PMMA system, the thermal conductivity was lower all the way. As soon the concentration of GNPs increased to 20 percent, the thermal conductivity of

PP/PMMA/GNPs was over the result of PP/GNPs slightly, to reach $0.699 \text{ W m}^{-1} \text{ K}^{-1}$. And from the whole graph we could see that the rate of thermal conductivity increased is gradually growing and had a large enhancement when the content was over 15 percent. However, the other formula displayed a different trend at same concentrations of graphene. At very low loading below 5 percent, the thermal conductivity was much higher than the former one, while with over 20 percent concentration of GNPs, the result was the lowest one these three samples. And the whole tendency of the graph was slowly increasing of the rate of thermal conductivity enhancement. The reason might be that PLA and PMMA are both polar matrices which can help non-polar graphene move into non-polar polymer matrix PP. However, PLA is a crystalline polymer, while PMMA is an amorphous one. In both blendings, PP formed the continuous phase which has more content than other two polymers. When low loading of graphene added into polymer blending, the random structure of PMMA might trap more graphene inside itself than the effect of ordered PLA made at the same content of GNPs. Hence, the concentration of graphene located in PP phase was lower in PP/PMMA system than the one in PP/PLA system, which caused the poor thermal conductivity at the beginning. On the other hand, if the graphene located inside the PLA matrix, the order structure of PLA could maintain the direction of graphene, which helped the enhancement of thermal conductivity. Then with the increase of additive, more effective heat conduction pathways could be formed in PP matrix or at the interface between PP and another polymer [29]. And when the concentration of nano-filler increased over 20 percent, the random close-packed structure of nanoparticles, which resulted in a large improvement of thermal conductivity for their ease formation of thermally

conducting pathways. Therefore, graphene could make a close-packed structure easily in amorphous PMMA than crystalline PLA, and the larger increase of thermal conductivity appeared in PP/PMMA/GNPs system with over 20 wt % GNPs added.

Table 11. Thermal conductivity of PP/PMMA/GNPs nanocomposites

Sample code	Concentrations (wt %)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
P1P2GNPs0	70/30/0	0.186
P1P2GNPs1	70/30/5	0.289
P1P2GNPs2	70/30/10	0.349
P1P2GNPs3	70/30/15	0.464
P1P2GNPs4	70/30/20	0.699

Table 12. Thermal conductivity of PP/PLA/GNPs nanocomposites

Sample code	Concentrations (wt %)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
P1P2GNPs0	60/40/0	0.214
P1P2GNPs1	57/38/5	0.457
P1P2GNPs2	54/36/10	0.516
P1P2GNPs3	51/34/15	0.590
P1P2GNPs4	48/32/20	0.622

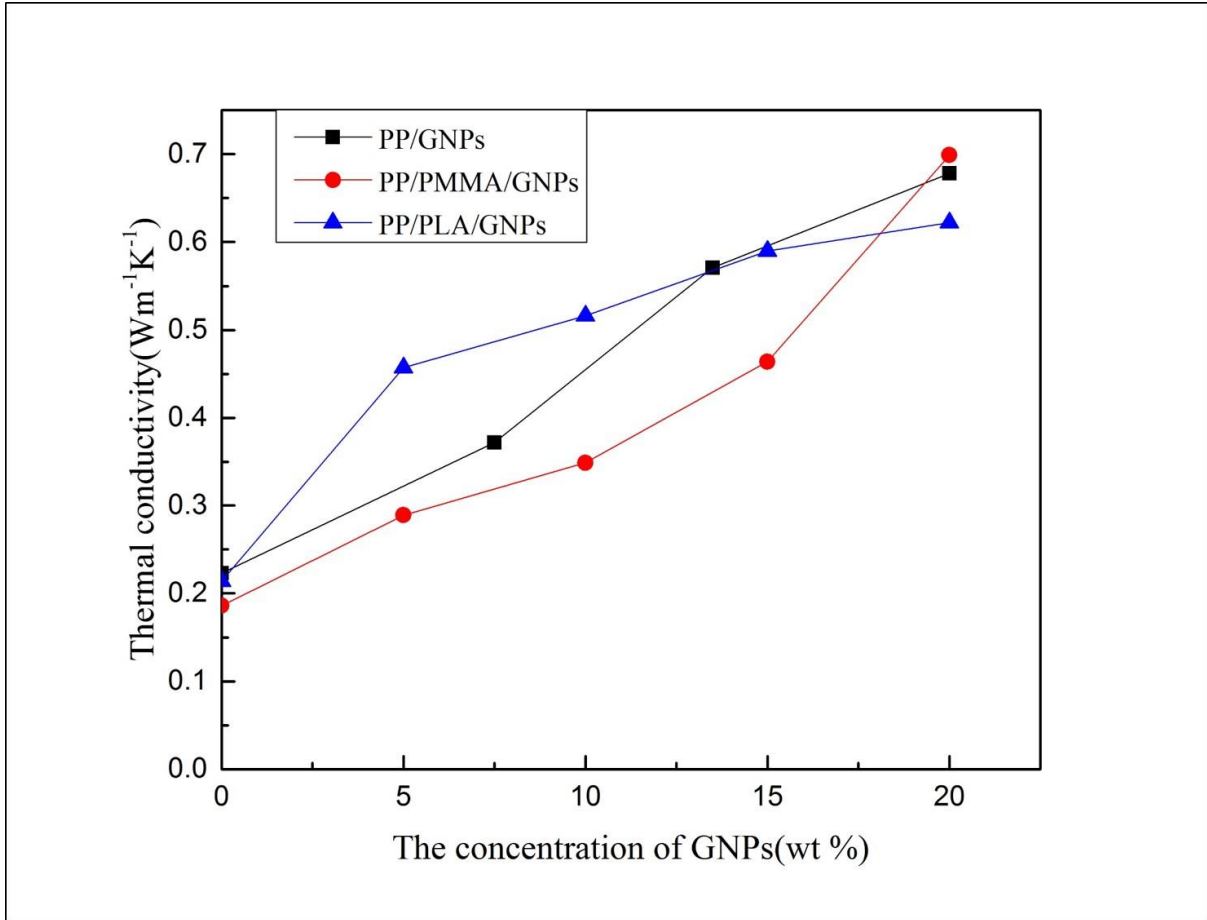


Figure 15. Thermal conductivity of PP nanocomposites

3.2.2 Thermal conductivity of PS nanocomposites

A similar analysis of PS/GNPs and PS/PMMA/GNPs was wrought with Figure 16. Pure polystyrene had only $0.180 \text{ W m}^{-1} \text{ K}^{-1}$ thermal conductivity, whereas PS/PMMA had a few higher result around $0.197 \text{ W m}^{-1} \text{ K}^{-1}$. As the increase added of graphene the results increased gradually and when the concentration reached to 20 percent, the thermal conductive value was jumping to $0.900 \text{ W m}^{-1} \text{ K}^{-1}$, approximately 5 times than the pure one. This is because PS is an amorphous polymer which has more random structure to store nano-fillers and help them have well dispersion. When the content of nanoparticles is lower, there are not enough heat

conduction pathways formed to transfer heat inside the polymer composites, even though the graphene disperses well without aggregation. If the concentration increased to 20 percent, more effective pathways formed and a dramatic increase of thermal conductivity would achieve as the experimental results shown. When PMMA mixed with PS/GNPs system, the thermal conductivity was higher than PS/GNPs with low loading of graphene because PMMA helped non-polar nano-filler located in PS phase or at the interface near PS side. Then the rate of increase was slowly than the former one because more part of graphene was trapped by PMMA and the effective conduction pathways might not form as much as before. Hence, with the content of graphene over 15 percent, the results were below the pure PS/GNPs system.

Table 13. Thermal conductivity of Ps/GNPs nanocomposites

Sample code	Concentrations (wt %)	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
PGNPs0	100/0	0.180
PGNPs1	95/5	0.267
PGNPs2	90/10	0.475
PGNPs3	85/15	0.527
PGNPs4	80/20	0.900

Table 14. Thermal conductivity of PS/PMMA/GNPs nanocomposites

Sample code	concentrations	Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
P1P2GNPs0	60/40/0	0.197
P1P2GNPs1	58.8/39.2/2	0.238
P1P2GNPs2	57.6/38.4/4	0.269
P1P2GNPs3	57/38/5	0.372
P1P2GNPs4	56.4/37.6/6	0.435
P1P2GNPs5	55.2/36.8/8	0.390
P1P2GNPs6	54/36/10	0.619
P1P2GNPs7	51/34/15	0.497
P1P2GNPs8	48/32/20	0.668

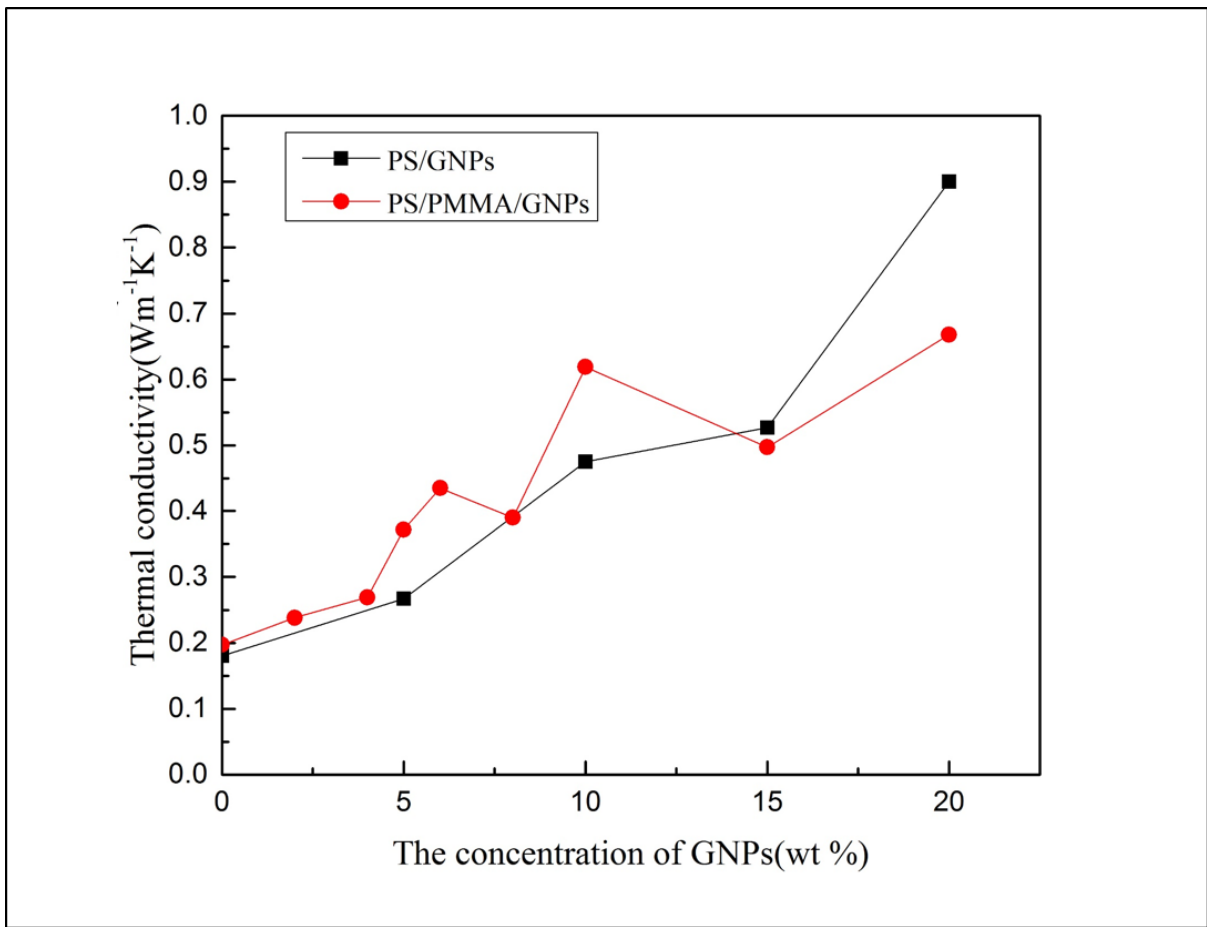


Figure 16. Thermal conductivity of PS nanocomposites

Chapter 4. Conclusion

To expand the applications of polymers, flame retardant is attractive more attention recently. Various additives have been proved to be effective on PLA flame retardancy in the study, we achieved several formula of PLA/nanoparticles composites which can successfully pass the V_0 level of UL-94 vertical burning test. The lowest ratio of nano-fillers contents to add in PLA and reach V_0 grade is 90 percent PLA mixed with 10 percent Ce-RDP, however, the mechanical properties like impact and tensile reduced heavily even could not make specimens by molding. With the concentration of MoS_2 below 15 percent, there was no flame retardant of PLA/ MoS_2 system, while when MoS_2 added over 20 percent, the dripping was heavily and combusted the cotton before self-extinguished. The best formula in our study to compromise the flame retardant and mechanical properties was 83 percent PLA combined with 15 percent MPP, 1 percent Ce-RDP and 1 percent C-20A, which passed UL-94 V_0 grade and had improved Young's modulus to 3.85 GPa. Moreover, further research will take to confirm a most effective way of PLA flame retardant. And we will do the cone calorimeter analysis and thermogravimetric analysis (TGA) to find the direct flame retardant mechanism and decomposition process during combusting.

Graphene (GNPs) and its modified are widely used in many aspects. One of the applications is to enhance the thermal conductivity of polymers. Graphene is a layered and dark colored powder with significant use in materials. During the research, we found that only low loading of graphene added could improve thermal conductivity effectively. And the rate of increase of thermal conductivity was related to the degree of crystallinity of polymer

matrices, the mixing time and temperature and also the similarity of polarization between polymers and nano-fillers. We can see a huge difference between the thermal conductivity through PP/GNPs nanocomposites and PS/GNPs nanocomposites. PS has a larger enhancement of thermal conductivity than PP because of the well random dispersion of graphene in an amorphous structure. And if we mix another polar polymer with PP or PS, the results of thermal properties are also improved by the attraction of similar polarization between polymer matrix and nano-fillers. However, it should be noted that the thermal conductivity of polymers depends on many complex factors and the prediction of the results presents a significant degree of complexity. Furthermore, we will do some transmission electron telescope (TEM) to directly discover the phase of most graphene located in, i.e. analyze the selective localization behavior of graphene.

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