

Stony Brook University



OFFICIAL COPY

The official electronic file of this thesis or dissertation is maintained by the University Libraries on behalf of The Graduate School at Stony Brook University.

© All Rights Reserved by Author.

**The flame retardant, mechanical properties, thermal properties and permeability of
biodegradable polymers**

A Thesis Presented

by

Xianghao Zuo

to

The Graduate School

in Partial Fulfillment of the

Requirements

for the Degree of

Master of Science

in

Materials Science and Engineering

Stony Brook University

May 2016

Stony Brook University

The Graduate School

Xianghao Zuo

We, the thesis committee for the above candidate for the
Master of Science degree, hereby recommend
acceptance of this thesis.

Miriam Rafailovich – Thesis Advisor

Distinguished Professor, Department of Materials Science and Engineering

Jonathon Sokolov – Second Reader

Professor, Department of Materials Science and Engineering

Tae Jin Kim – Third Reader

Assistant Professor, Department of Materials Science and Engineering

This thesis is accepted by the Graduate School

Charles Taber
Dean of the Graduate School

**The flame retardant, mechanical properties, thermal properties and permeability of
biodegradable polymers**

by

Xianghao Zuo

Master of Science

in

Materials Science and Engineering

Stony Brook University

2016

Abstract

Nano-particles are great additives to the thermal properties of the polymers, however, they sometimes have some disadvantages on the mechanical properties. The mixing of polymers and nano-particles such as cloisite clays, graphene, melamine polyphosphate and molybdenum disulfide, are mostly physical reactions between them. Therefore, the dispersion of the nano-particles inside the polymers is very important. As for the flame retardant of the polymers, the additives are used as three most important components during the mixing, i.e. the acid source, the carbonization agent (or char forming agent), and a blowing agent. The better the particles disperse in the polymer, the easier the material will blow and form chars during the combustion. Some of the nano-particles are used for heat conduction, which means if they have a better thermal conductivity and are better dispersed in the polymer, will certainly be benefit for the flame retardant. On the other hand, as for the gas permeability of the material, which means the gas diffuses through the polymer. Permeation is something that must be regarded highly in various

polymer applications, due to their high permeability. Permeability depends on the temperature of the interaction as well as the characteristics of both the material and the permeant component. For pure polymers, since there is no additives and due to their own defects of the microstructure, gas will easily diffuse via the defects of the polymers. However, when nano-particles are mixed with the polymer, they will form barriers in the polymer and will make the gas to go a further path when it diffuses in a polymer. Hence, the well disperse of the nano-particles will be one of the key elements to reduce the gas permeation of the polymer and another factor which will impact the results will be the length over the width of the barriers. During the whole research, we focused on the most popular polymers like high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) and poly (lactic acid) (PLA). And the nanoparticles we used are, cloisite clays, graphene (GNPs), melamine polyphosphate (MPP), and molybdenum disulfide (MoS_2). We successfully obtained some materials which have excellent flame retardancy properties. We also get some materials that reduce the gas permeation with the help of these nanoparticles. In this paper, we studied and demonstrated the MPP is a great agent when mixed with PLA and become an excellent self-extinguish material, which can achieve the request of V_0 of UL-94 test. We demonstrated that, when PP is mixed with MoS_2 , MoS_2 has a good dispersion in PP, so it is helpful to reduce the gas diffusion in PP, this will be proved by the scanning electron microscope (SEM) test. As it is known, crystallinity plays an important role to affect the gas permeation, we did differential scanning calorimetry (DSC) to calculate the crystallinity and study the migration of the melting temperature of PP/ MoS_2 system. Furthermore, we also test the mechanical properties of these materials such as Izod test which can provide the impact strength of the materials and tensile test which can help us with the modulus of the materials. We found that the modulus of PP/ MoS_2 system is enhanced and the impact strength is maintained.

Table of Contents

Abstract	iii
List of Figures	vi
List of Tables	viii
List of Abbreviations	ix
Acknowledgments.....	xi
Chapter 1 Introduction	1
Chapter 2 Experimental Section	6
2.1 Materials.....	6
2.2 RDP coated C-Na ⁺ (C-RDP) and Cellulose (Ce-RDP) preparation.....	6
2.3 Nanocomposites preparation	7
2.4 Characterization Methods	8
2.4.1 Scanning electron microscope (SEM)	8
2.4.2 Dynamic mechanical test.....	10
2.4.3 Differential scanning calorimetry (DSC)	10
2.4.4 Mechanical tests	10
2.4.5 Gas Permeability tests	11
Chapter 3. Results and discussion.....	17
3.1 Results and discussion of PLA/nanocomposites flame retardant tests	17
3.2 Results and discussion of clays, HNTs, GNPs and MoS ₂ polymer nanocomposites.....	21
3.2.1 Microstructure of nanocomposites	21
3.2.2 Mechanical Properties	23
3.2.3 Dynamic mechanical analysis	37
3.2.4 Differential scanning calorimetry.....	39
3.2.5 Oxygen gas permeability	42
Chapter 4 Conclusion.....	48
References.....	50

List of Figures

Figure 1. C-20A structure	2
Figure 2. C-30B structure	2
Figure 3. Resorcinol di (phenyl phosphate) (RDP)	3
Figure 4. MPP structure.....	5
Figure 5a. Brabender, Figure 5b. Hot Pressure	8
Figure 6. Images of the preparation of SEM tests: (a) HDPE/C-RDP nanocomposites, (b) PP/MoS ₂ nanocomposites	9
Figure 7a. Tensile test machine, Figure 7b. IZOD impact test machine	11
Figure 8. Gas permeability test facility	12
Figure 9. SEM image of nanocomposites: (a) 100HDPE2C-RDP, (b) 100HDPE4C-RDP, (c) 100HDPE6C-RDP, (d) 100PP2MoS ₂ , (e) 100PP4MoS ₂ , (f) 100PP6MoS ₂ , (g) 100PP6MoS ₂ , (h) HNTs, (j) H-RDP.	22
Figure 10. Young's Modulus of HDPE/clay nanocomposites	24
Figure 11. Young's Modulus of LDPE/clay nanocomposites.....	25
Figure 12. Young's Modulus of PP/MoS ₂ nanocomposites.....	26
Figure 13. Elongation at break of HDPE/clay nanocomposites	29
Figure 14. Tensile strength of HDPE/clay nanocomposites.....	29
Figure 15. Elongation at break of LDPE/clay nanocomposites.....	30
Figure 16. Tensile strength of LDPE/clay nanocomposites	31
Figure 17. Elongation at break of PP/MoS ₂ nanocomposites.....	32
Figure 18. Tensile strength of PP/MoS ₂ nanocomposites	32
Figure 19. Impact strength of HDPE/clay nanocomposites	35
Figure 20. Impact strength of PP/clay nanocomposites	36
Figure 21. DMA results of HDPE/C-RDP nanocomposites: (a). Storage modulus, (b) Tan Delta	38

Figure 22. DSC results of HDPE/C-RDP nanocomposites	40
Figure 23. DSC results of PP/MoS ₂ nanocomposites.....	41
Figure 24. Ideal layered platelets and the oxygen diffusion pathway	43
Figure 25. Ideal oxygen diffusion pathway of nanotubes	44
Figure 26. Oxygen permeability of nanocomposites with different volume fraction of clays. The dash-dot lines represents the fitting results of polymer nanocomposites according to the Nielsen model. (a) HDPE/clay, (b) LDPE/clay, (c)PLA/clay, (d) PLA/nanotubes, (e) PP/clay.....	45

List of Tables

Table 1. Concentrations of nanocomposites used for PLA flame retardant test	13
Table 2. Concentrations of nanocomposites used for PLA gas permeability test	14
Table 3. Concentrations of nanocomposites used for HDPE gas permeability test	15
Table 4. Concentrations of nanocomposites used for LDPE gas permeability test.....	15
Table 5. Concentrations of nanocomposites used for PP gas permeability test	16
Table 6. UL-94 tests of PLA nanocomposites.....	19
Table 7. Young's modulus results of HDPE/clay nanocomposites.....	24
Table 8. Young's Modulus results of LDPE/clay nanocomposites.....	25
Table 9. Young's Modulus results of PP/MoS ₂ nanocomposites.....	26
Table 10. Elongation results and tensile strength of HDPE/clay nanocomposites.....	28
Table 11. Elongation results and tensile strength of LDPE/clay nanocomposites	30
Table 12. Elongation results and tensile strength of PP/MoS ₂ nanocomposites	31
Table 13. Impact strength of HDPE/clay nanocomposites.....	35
Table 14. Impact strength of PP/clay nanocomposites.....	36
Table 15. Glass transition temperatures (T _g) of HDPE/C-RDP nanocomposites.....	38
Table 16. Crystallinity and melting temperature of HDPE/C-RDP nanocomposites.....	40
Table 17. Crystallinity and melting temperature of PP/MoS ₂ nanocomposites	41

List of Abbreviations

C-Na⁺: Closite sodium

C-20A: Closite 20A

C-30B: Closite 30B

RDP: Resorcinol di (phenyl phosphate)

C-RDP: Mixing of closite sodium and RDP

Ce-RDP: Mixing of Cellulose and RDP

MoS₂: Molybdenum disulfide

GNPs: Graphene

MPP: Melamine polyphosphate

PLA: Poly (lactic acid)

HDPE: High density polyethylene

LDPE: Low density polyethylene

PP: Polypropylene

PS: Polystyrene

PMMA: Poly (methyl methacrylate)

SEM: Scanning electron microscope

DSC: Differential scanning calorimetry

DMA: Dynamic mechanical analysis

T_m: Melting point

T_g: Glass transition temperature

IFR: Intumescent flame retardant

NG: None grade

pHRR: Peak heat release rate

Acknowledgments

I would like to sincerely thank my advisor, Professor Miriam Rafialovich, for giving me a chance to work with her. During the research, she really gave me a lot of guidance and suggestions. Since I was a freshmen from this group, she always encouraged me and approved my work. Her kind, encouragement and advising always made me confident in the study.

I would appreciate Dr. Chung-Chueh Chang from Advanced Energy Center, who helped me with lots of tests and gave me the chance to get more accurate results via using the instruments in the energy center.

A specimen thanks to Yichen Guo and Yuan Xue, for helping me all the time during my research.

Finally, I would like to thanks my parents for always supporting me and for their love.

Chapter 1 Introduction

In the recent years, since the deterioration of the quality of the air situation and the growing pollution hazards, recyclable plastics, which are regarded to be more environmental friendly, are widely used to meet the demand in both cutting the costs and protecting the environment. Poly (lactic acid) (PLA), Polyethylene (PE) and Polypropylene (PP) are most common polymers and they rarely produce contaminations as they are in the plastic identification code system. Currently, in the Society of the Plastic Industry (SPI) plastic identification code, 2 is for HDPE, 4 is for LDPE, 5 is for PP and for PLA, which is a biodegradable polymer, we can consider it as 7 [1]. According to the advantage of cheap, light in the weight and also easily to form the shape, more and more diverse applications are applied on these polymers, which means they become pliable or moldable above a specific temperature and solidifies upon cooling [2]. Therefore, with the technique of hot pressing, we can obtain the specimen we need and do the tests with different types of specimen. HDPE is known for its large strength-to-density ratio. The most common property of these four kinds of polymers is that they are all thermoplastic polymers. As HDPE has little branching, it has stronger intermolecular forces and tensile strength when compared to LDPE. LDPE has more branches than HDPE, so it is more flexible and its resilience is higher. PP is the commodity plastic with the lowest density. It is normally tough and flexible, which allows PP to be used as an engineering plastic. And it also has good resistance to fatigue [3]. PLA is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, such as corn starch, tapioca roots, chips or starch, or sugarcane. Hence, these polymers have a broad market prospect to act as a potential replacement to the old materials. Besides these advantages of polymer materials, further consideration has been carried out to improve the modulus, reduce the gas permeation and flammability. It has been proved that nano-particles like organically modified

montmorillonite (MMT) clays can effectively help to increase the thermal properties, modulus and even gas barriers when mixed into the polymer [4-6]. The degree of material properties strengthened were related to the degree of exfoliation of MMT. A well exfoliated material should be regarded as the MMT to be divided into numerous sections and homogeneously dispersed in the polymer. As the mixing of MMT and polymers are a physical reaction, the dispersion also depends on the surface energy between polymers and the surface of clays. As improvements of the basic C-Na⁺ clay, C-20A and C-30B are actually acquired via the cation exchange with quaternary ammonium chloride salts. The structure of C-20A and C-30B are shown in figure 1 and figure 2, respectively. They are highly toxic and will release toxic chemicals under higher operating temperatures. Therefore, some more environmental friendly additives were suggested as replacements of these clays and they can achieve improvement of the material as well.

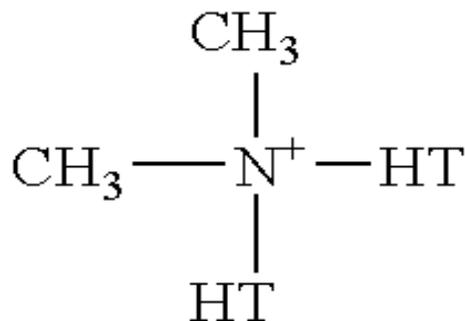


Figure 1. C-20A structure

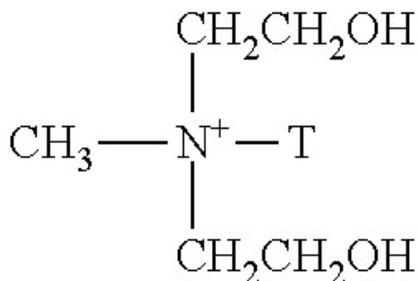


Figure 2. C-30B structure

According to figure 3, the structure of resorcinol di (phenyl phosphate) (RDP), which is much safer than ammonium chloride salts, can be coated on C-Na⁺ and form C-RDP clay. Pack et al. have proved that RDP absorbed clay owns an advantage of large exfoliation in some polymer like polystyrene [7]. In this paper, we studied the properties of C-RDP mixed with PLA and HDPE. Furthermore, RDP coated cellulose is also made as Ce-RDP to do the flame retardant test, since even under the combustion state, it will not release any toxic gas. RDP is a good flame retardant, however, it is a liquid, so it usually coated with other solid materials. The easy coating and well dispersion make it an effective additive as a barrier in the polymer and might reduce the gas diffusion.

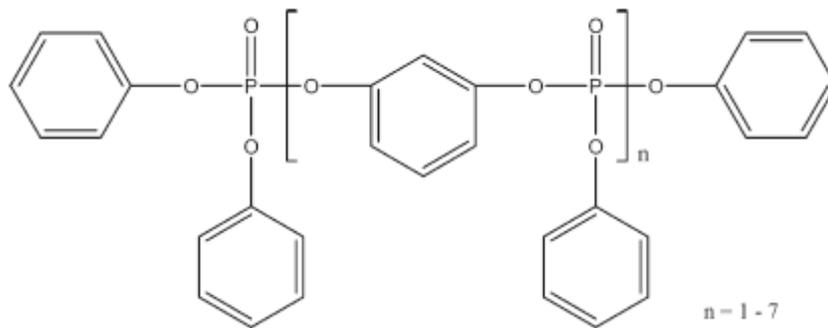


Figure 3. Resorcinol di (phenyl phosphate) (RDP)

Graphene (GNPs) is a unique material that has a number of particular properties. It is about 100 times stronger than the strongest steel with a hypothetical thickness of 3.35Å which is equal to the thickness of the graphene sheet [8]. It can efficiently conduct heat and electricity, so we consider it might be useful to reduce the flammability of the polymer because it can easily conduct heat, and when one side of the specimen was combusted, graphene can help conduct the heat to the other side of the specimen so the temperature will not meet the ignition point. Ramanathan et al. reported the improvement of the mechanical and thermal properties of polymethyl methacrylate

(PMMA) with the addition of 1 wt.% of thermally reduced graphene[9]. PMMA is a polar polymer, and here, our samples, PP has lower polarity and PE is non-polar. Graphene was mixed with PP and PE for the gas permeability and mechanical test to see how graphene acts in these polymers.

Molybdenum disulfide (MoS_2) is a metal dichalcogenide, Most of time, MoS_2 is a stable material, and it's relatively unreactive. MoS_2 has been used as a solid lubricant for a long time. MoS_2 nanosheets, like graphene, is gradually used as an additive to enhance the polymer in recent years. Z. Matusinovic et al have proved that MoS_2 is effective for promoting thermal stability in PMMA matrix [10]. X. Feng et al have documented MoS_2 has excellent barrier performance in PP, it can reinforce thermal oxidative stability and reduce flammable pyrolysis gas [11]. Therefore, we mixed MoS_2 with PP and PE. The samples were used for gas permeability tests, tensile tests, Izod impact tests and also SEM tests. Due to the difference in the dispersion of MoS_2 in PP and PE, they showed us different results. SEM images of PP/ MoS_2 nanocomposites provide us an outstanding exfoliate of MoS_2 in PP.

As an environmental protection type non-halogen flame retardant, melamine polyphosphate (MPP) is widely used as a flame retardant to blend with series of polymers. MPP belongs to a class of materials known as char-forming or intumescent flame retardants [12]. S. Jahromi et al certificated that MPP acts by forming a barrier layer of char during the combustion process and phosphoric acid is believed to be the active center (catalyst) in MPP. Thermal stability of polymers is influenced dramatically by the presence of MPP [13]. We also obtained this result when doing the flame retardant test of PLA/MPP nanocomposites. Different mass ratios of PLA and MPP were mixed and undergone UL-94 test. The structure of MPP is shown in figure 4.

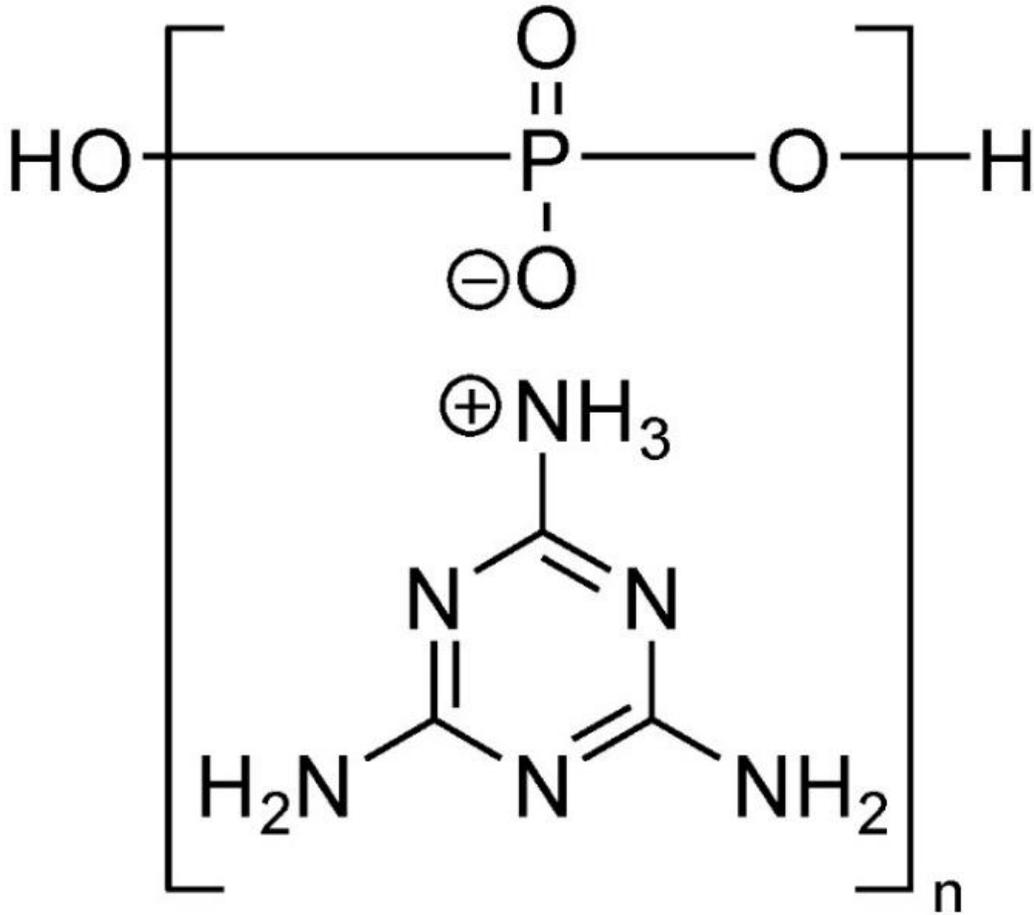


Figure 4. MPP structure

Chapter 2 Experimental Section

2.1 Materials

The MMT-clays, Cloisite Na⁺ (C-Na⁺) and organoclays, Cloisite 30B (C-30B), Cloisite 20A (C-20A) were supplied by Southern Clay Inc. C-20A is a natural montmorillonite modified with N,N-dimethyl dehydrogenated tallow quaternary ammonium chloride. C-30B is synthesized via ion exchange between Na⁺ of the C-Na⁺ and bis (2-hydroxyethyl) methyl hydrogenated tallow quaternary ammonium cation. The RDP, known as Fyrolflex RDP, was a type of phosphorus flame retardant agent (FR) provided by ICL-IP Inc. Poly (lactic acid), PLA 4042D, was purchased from the Natureworks LLC with a density of 1.24 g/cm³ and molecular weight of 120000 g/mol. High density polyethylene, HDPE 2710, was purchased from Naomi Stewart[®] with a density of 0.951 g/cm³. Low density polyethylene, LDPE 1007, was purchased from Amco Polymers[®] with a density of 0.917 g/cm³. Polypropylene, PP 3825, was purchased from Amco Polymers[®] with a density of 0.905 g/cm³. Graphene C-750 was purchased from XG Sciences' xGNP[®] with a density of 2.1 g/cm³. Molybdenum disulfide (MoS₂) was purchased from Sigma-Aldrich[®] with a density of 5.06 g/cm³. Melamine polyphosphate (MP) was purchased from Boc Sciences[®].

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

To prepare C-RDP, 20wt % of RDP was placed in a 200 mL baker and heated on a heat plate at 70 °C. Then 80wt % of C-Na⁺ was added stirred manually with RDP for about 10 minutes. And then the mixture should be transferred to a plastic sample holder, which should be insert into a Thinky Mixer for further mixing. The procedure was set at 700 rpm and 5 min. After that, the mixture should be taken out and put into a mortar to be grinded. Then the mixture was put into the

Thinky Mixer and repeat this procedure for several times until it is mixed as a uniform part. Finally, the mixture was transferred back to the 200 mL baker and placed in a vacuum oven at 70 °C for over 24 hours in order to remove the moisture and complete the RDP coating. We have the same procedure for the preparation of Ce-RDP, but the ratio of cellulose and RDP would change to 40wt % of RDP and 60wt % of cellulose.

2.3 Nanocomposites preparation

The nanocomposites were prepared with the method of melting blend in the C.W. Brabender. Since the difference of the melting temperature of polymers, the operating temperature was set at 160 °C for PLA, HDPE and LDPE, while 180 °C for PP, as PP has higher melting point. Polymer pellets and nano-particles were added into the chamber at 20 rpm and when the pellets were melted, the speed was increased to 100 rpm. The mixing takes 10 mins for each sample. Then we take out the samples and cut them into small pieces to be able to fill in the modes. The molding was carried out in a hot-pressure at the temperature of 180 °C. The ratios of the samples for the flame retardancy test are shown in Table 1, while the samples for gas permeability test are shown in Table 2 – Table 5. The brabender and hot-pressure is shown in Figure 5a-b.

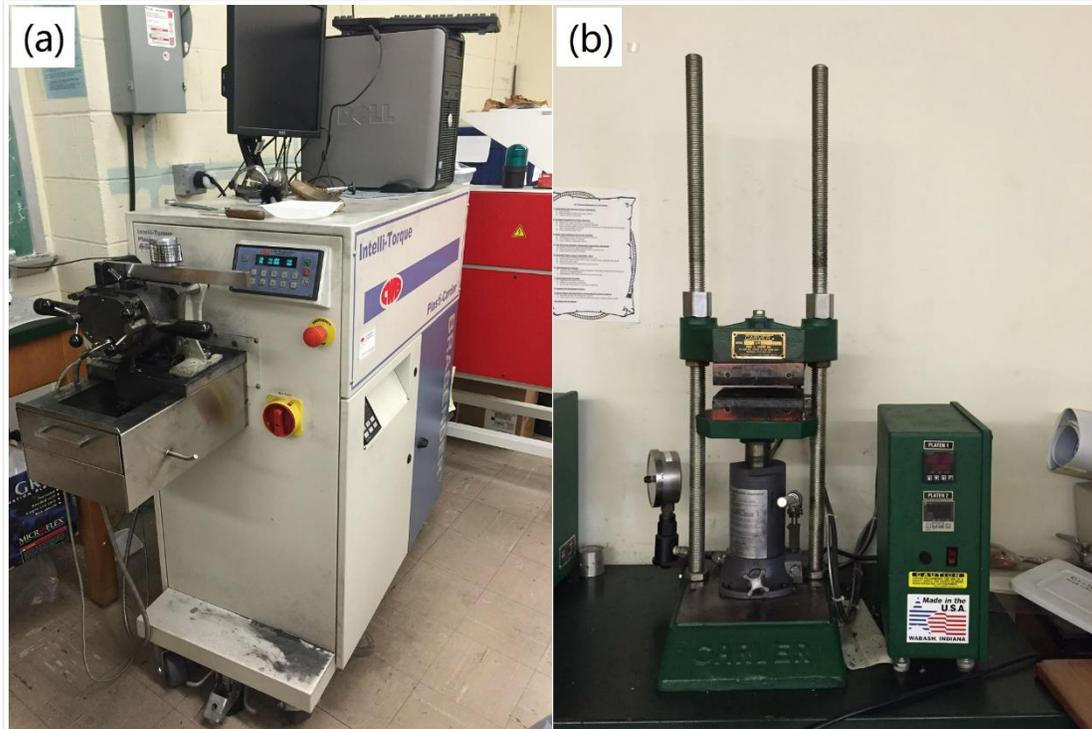


Figure 5a. Brabender, Figure 5b. Hot Pressure

2.4 Characterization Methods

2.4.1 Scanning electron microscope (SEM)

The SEM (Jeol JSM7600F) with a Schottky electron gun was used to display the fracture surfaces of the broken impact samples. The elemental distribution of silicon, aluminum and sodium were respectively acquired using an Energy Dispersive X-ray Spectroscopy (EDXS) attachment on the SEM. All the samples were required to coat 10 nm thickness of gold on the surfaces to increase electrical conductivity. Figure 6a-b shows the SEM tests of HDPE/C-RDP nanocomposites and PP/MoS₂ nanocomposites.

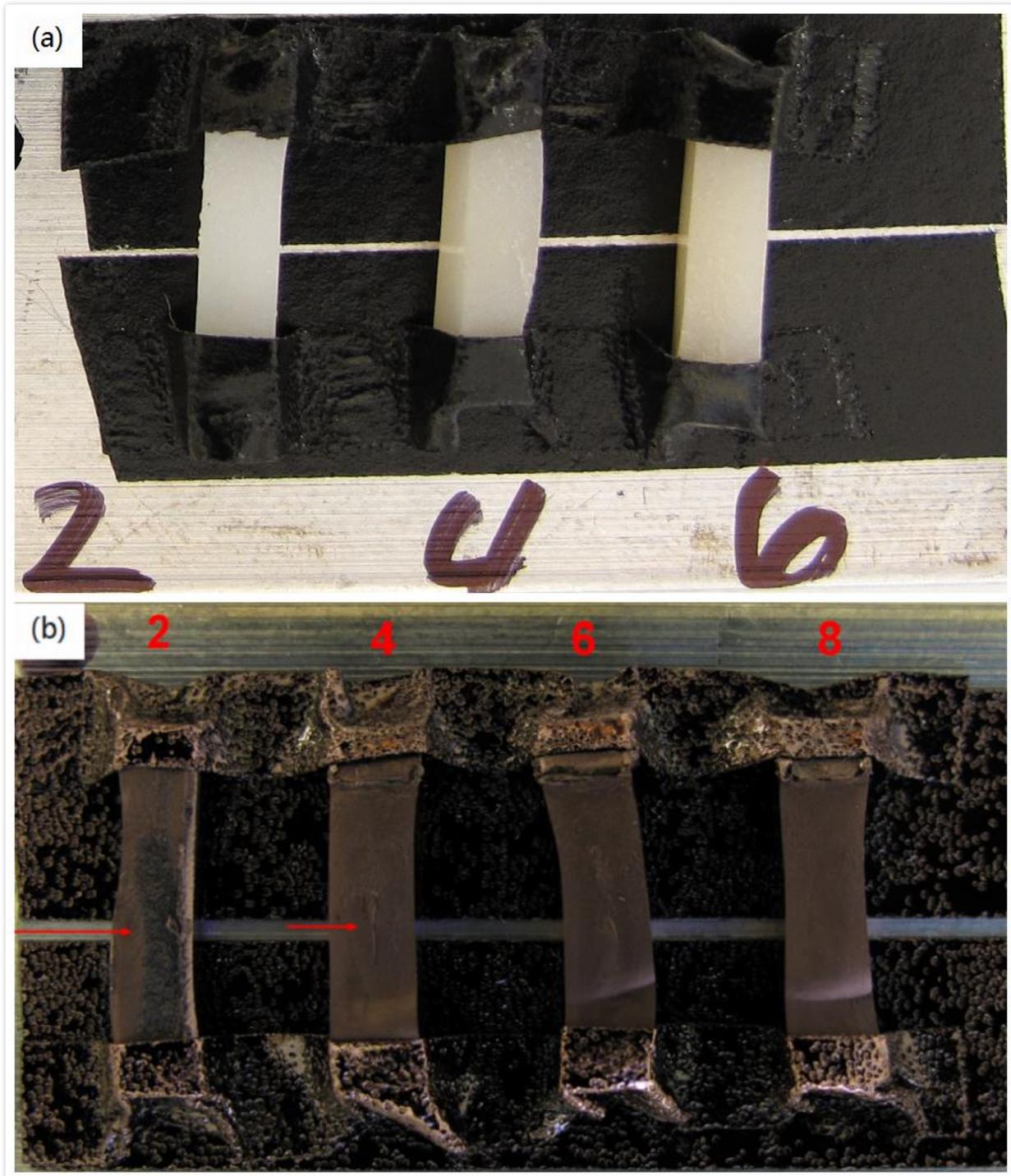


Figure 6. Images of the preparation of SEM tests: (a) HDPE/C-RDP nanocomposites, (b) PP/MoS₂ nanocomposites

2.4.2 Dynamic mechanical test

TA Instruments DMA Q800 was used to perform the dynamic mechanical properties of nanocomposites under the single cantilever bend mode at the frequency of 1 Hz. The storage modulus and $\tan \delta$ were collected from -130 to 100 °C at the rate of 3 °C/min.

2.4.3 Differential scanning calorimetry (DSC)

TA Instruments DSC Q2000 was used to obtain the heat flux over temperature and time of the samples. The results of heat flow over temperature and time were collected from 20 to 200 °C at the rate of 10 °C/min for HDPE/C-RDP and from 40 to 200 °C at the rate of 10 °C/min for PP/MoS₂.

2.4.4 Mechanical tests

Instron 5542 (Instron Co., Grove City, PA) was used to advance the tensile properties test, this instrument was used in compliance with ASTM D-638, type M. For HDPE and PP samples, the extension rate was set as 2 mm/min. while for LDPE samples, the extension rate was set as 20 mm/min since they are more flexible. Monitor/Impact Testing Machines Inc. is used to carry on Izod impact tests. The Izod impact tests are according to ASTM D-256 test method. 10 specimens of each sample were tested to obtain the average value for the impact strength. Figure 7a-b shows the tensile and IZOD impact test machine.

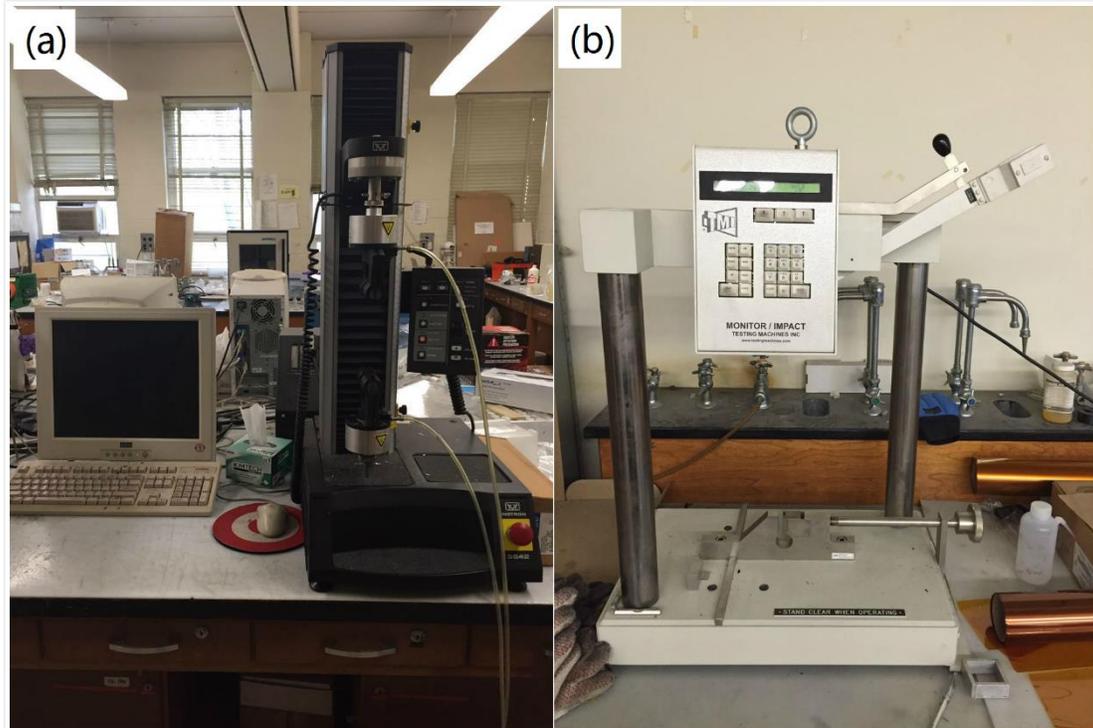


Figure 7a. Tensile test machine, Figure 7b. IZOD impact test machine

2.4.5 Gas Permeability tests

A permeability cell apparatus (CSI-135, Custom Scientific Instruments, Inc.) is used to test the oxygen diffusion through the materials under ASTM D-1434 standard. Two different thickness of specimens were made for different polymers. The two thicknesses are 0.078 cm and 0.165 cm, respectively. They were made by hot pressing. Five and more tests were conducted to calculate the average of the results. The facility used to carry on gas permeability test is shown as Figure 8.

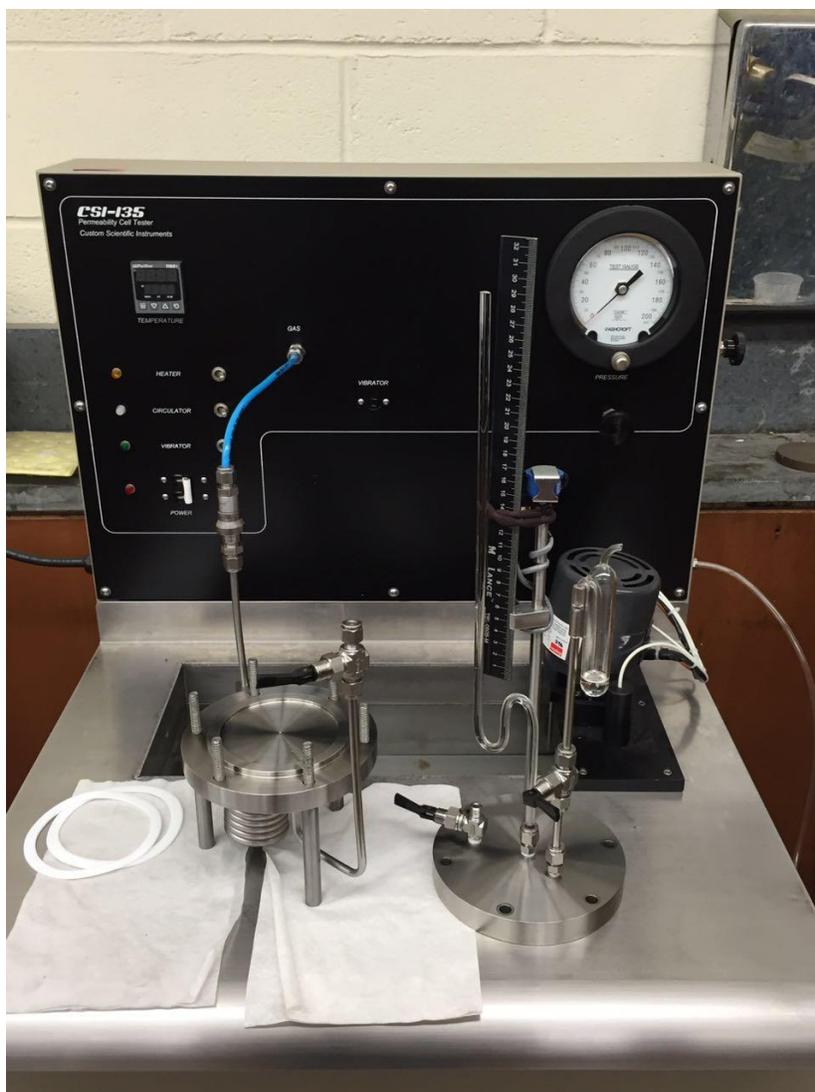


Figure 8. Gas permeability test facility

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

Sample Code	PLA (%)	MPP (%)	MPP-RDP (%)	Ce (%)	Ce-RDP (%)	C-20A (%)	C-30B (%)	C-RDP (%)
PMMP1	70	30	0	0	0	0	0	0
PMMP2	75	25	0	0	0	0	0	0
PMMP3	80	20	0	0	0	0	0	0
PMMP4	85	15	0	0	0	0	0	0
PMMP5	90	10	0	0	0	0	0	0
PMMPCe1	70	20	0	10	0	0	0	0
PMMPCe2	80	10	0	10	0	0	0	0
PCeRDP1	85	0	0	0	15	0	0	0
PCeRDP2	88	0	0	0	12	0	0	0
PCeRDP3	90	0	0	0	10	0	0	0
PCeRDP4	92	0	0	0	8	0	0	0
PCeRDP5	95	0	0	0	5	0	0	0
PMMPCeRDP1	70	20	0	0	10	0	0	0
PMMPCeRDP2	75	20	0	0	5	0	0	0
PMMPCeRDP3	80	15	0	0	5	0	0	0
PMMPCeRDP4	80	10	0	0	10	0	0	0
PMMPCeRDP5	83	12	0	0	5	0	0	0
PMMPRDP1	80	0	20	0	0	0	0	0
PMMPRDP2	85	0	15	0	0	0	0	0
PMMPC20A1	84	15	0	0	0	1	0	0
PMMPC20A2	85	12	0	0	0	3	0	0
PMMPC20A3	85	13	0	0	0	2	0	0
PMMPC20A4	88	10	0	0	0	2	0	0
PMMPCeRDPC20A1	83	15	0	0	1	1	0	0
PMMPCeRDPC20A2	84	12	0	0	3	1	0	0
PMMPCeRDPC20A3	85	12	0	0	2	1	0	0
PMMPRDPCRDP	84	0	15	0	0	0	0	1
PCeRDPC30B1	86	0	0	0	13	0	1	0
PCeRDPC30B2	87	0	0	0	12.5	0	0.5	0
PCeRDPC30B3	87	0	0	0	12	0	1	0
PCeRDPC20A	87	0	0	0	12	1	0	0

Table 2. Concentrations of nanocomposites used for PLA gas permeability test

Sample	PLA (%)	C- Na⁺ (%)	C-RDP (%)	HNTs (%)	H-RDP (%)	C-20A (%)
PLA	100	0	0	0	0	0
PLACNa⁺1	100	1	0	0	0	0
PLACNa⁺2	100	3	0	0	0	0
PLACNa⁺3	95	5	0	0	0	0
PLACNa⁺4	100	7	0	0	0	0
PLACNa⁺5	90	10	0	0	0	0
PLACRDP1	100	0	1	0	0	0
PLACRDP2	100	0	3	0	0	0
PLACRDP3	95	0	5	0	0	0
PLACRDP4	100	0	7	0	0	0
PLACRDP5	90	0	10	0	0	0
PLAHNTs1	100	0	0	1	0	0
PLAHNTs2	100	0	0	3	0	0
PLAHNTs3	95	0	0	5	0	0
PLAHNTs4	100	0	0	7	0	0
PLAHNTs5	90	0	0	10	0	0
PLAHRDP1	100	0	0	0	1	0
PLAHRDP2	100	0	0	0	3	0
PLAHRDP3	95	0	0	0	5	0
PLAHRDP4	100	0	0	0	7	0

Table 3. Concentrations of nanocomposites used for HDPE gas permeability test

Sample	HDPE (%)	C- Na ⁺ (%)	C-RDP (%)	C-20A (%)	C-E06 (%)	GNPs (%)
HDPE	100	0	0	0	0	0
HDPECNa ⁺ 2	100	2	0	0	0	0
HDPECNa ⁺ 4	100	4	0	0	0	0
HDPECNa ⁺ 6	100	6	0	0	0	0
HDPECRDP2	100	0	2	0	0	0
HDPECRDP4	100	0	4	0	0	0
HDPECRDP6	100	0	6	0	0	0
HDPEC20A2	100	0	0	2	0	0
HDPEC20A4	100	0	0	4	0	0
HDPEC20A6	100	0	0	6	0	0
HDPECE2	100	0	0	0	2	0
HDPECE4	100	0	0	0	4	0
HDPECE6	100	0	0	0	6	0
HDPEG2	100	0	0	0	0	2
HDPEG4	100	0	0	0	0	4
HDPEG6	100	0	0	0	0	6

Table 4. Concentrations of nanocomposites used for LDPE gas permeability test

Sample	LDPE (%)	C- Na ⁺ (%)	C-RDP (%)	C-20A (%)	GNPs (%)
LDPE	100	0	0	0	0
LDPECNa ⁺ 1	100	1	0	0	0
LDPECNa ⁺ 3	100	3	0	0	0
LDPECNa ⁺ 5	100	5	0	0	0
LDPECRDP1	100	0	1	0	0
LDPECRDP3	100	0	3	0	0
LDPECRDP5	100	0	5	0	0
LDPEC20A1	100	0	0	1	0
LDPEC20A3	100	0	0	3	0
LDPEC20A5	100	0	0	5	0
LDPEG1	100	0	0	0	1
LDPEG3	100	0	0	0	3
LDPEG5	100	0	0	0	5

Table 5. Concentrations of nanocomposites used for PP gas permeability test

Sample	PP (%)	MoS₂ (%)	GNPs (%)
PP	100	0	0
PPMoS₂2	100	2	0
PPMoS₂4	100	4	0
PPMoS₂6	100	6	0
PPMoS₂8	100	8	0
PPG2	100	0	2
PPG4	100	0	4
PPG6	100	0	6
PPG8	100	0	8

Chapter 3. Results and discussion

3.1 Results and discussion of PLA/nanocomposites flame retardant tests

The main purpose of this project is to find some additives which are benefit for the flame retardant of PLA [14-16]. PLA is a flammable polymer which has been used widely for decays. However, its poor flame retardant property sometimes limits its application. Therefore, to get a reasonable approach to improve the flame retardant of PLA is the current issue to be resolved. The former research of PLA/starch biocomposites which are studied by X. Wang et al, showed that 20 percent of intumescent flame retardant (IFR) and 10 percent of starch or 25 percent of Intumescent flame retardant and 5 percent of starch should be mixed with PLA so they can pass UL-94 V₀ grade [17]. J. Feng et al documented that at least 20 percent of β -cyclodextrin/ammonium polyphosphate/melamine complexes need to be added to PLA to get a V₀ grade [18]. In this study, we tried melamine polyphosphate (MPP) as an IFR which is both an acid source and a blowing agent. During the research, we certified that MMP can greatly help to reduce the combustion properties of PLA. Moreover, the percentage of MMP can be less than 20 percent, which seems to be an improvement to the previous studies since the total amount of IFR reduce to less than 20 percent. And MPP can help maintain the mechanical properties at the same time, while for some other particles like organically modified montmorillonite (MMT), are not good for the physical mechanical properties of polymers. According to UL-94 tests, V₀ means burning stops within 10 seconds on a vertical specimen; drips of particles allowed as long as they are not inflamed. A more detailed explanation is the specimens must be extinguished in 10 seconds and dripping is allowed but it can't ignite the cotton. However, most of the drips can ignite the cotton because when dripping is occurring, the drips always will have a high temperature and is flammable. Thus, we

tried to mix C-20A and C-30B with PLA/MPP system to keep the specimen from dripping when burning. Cellulose is a biodegradable polymer and it can degrade in the process of combustion and this procedure will release a lot of heat. When dripping occurs, most of the released heat will be dispersed into the air. Therefore, the dripping will not ignite the cotton. But the released heat will help the degrading of cellulose, and the pyrolysis products diffuse to the air and mix with oxygen so that combustion may take place around the specimen, which means it will take longer time to extinguish. That is why cellulose is not well performed as MMP, however, when mixed with RDP, it worked better. RDP alone is a liquid, it will create more drips during the combustion. As mentioned before, the drips can take away a lot of heat from the specimen. So RDP coated cellulose, Ce-RDP, is another system which will help PLA to enhance flame retardancy. The results of UL-94 tests are listed in Table 6.

Table 6. UL-94 tests of PLA nanocomposites

Sample	t₁ (s)	t₂ (s)	Dripping	Cotton combustion	UL-94 grade
PMMP1	0	2	N	N	V ₀
PMMP2	0	2	N	N	V ₀
PMMP3	0	5	N	N	V ₀
PMMP4	0	4	Y	Y	V ₂
PMMP5	0	3	Y	Y	V ₂
PMMPCe1	0	20	N	N	V ₁
PMMPCe2	0	0	Y	N	V ₀
PCeRDP1	>30		Y	N	NG
PCeRDP2	2	1	Y	Y	V ₂
PCeRDP3	1	15	Y	Y	V ₂
PCeRDP4	>30		Y	Y	NG
PCeRDP5	>30		Y	Y	NG
PMMPCeRDP1	1	1	N	N	V ₀
PMMPCeRDP2	0	2	N	N	V ₀
PMMPCeRDP3	1	1	N	N	V ₀
PMMPCeRDP4	2	10	N	N	V ₀
PMMPCeRDP5	>30		Y	Y	NG
PMMPRDP1	0	0	Y	N	V ₀
PMMPRDP2	8	3	Y	Y	V ₂
PMMPC20A1	0	5	N	N	V ₀
PMMPC20A2	>30		N	N	NG
PMMPC20A3	>30		N	N	NG
PMMPC20A4	>30		Y	Y	NG
PMMPCeRDPC20A1	1	1	N	N	V ₀
PMMPCeRDPC20A2	3	3	Y	Y	V ₂
PMMPCeRDPC20A3	4	8	Y	Y	V ₂
PMMPRDPCRDP	3	4	Y	Y	V ₂
PCeRDPC30B1	20		Y	Y	NG
PCeRDPC30B2	7	9	Y	Y	V ₂
PCeRDPC30B3	16	>30	Y	Y	NG
PCeRDPC20A	11	2	Y	Y	V ₂

According to Table 6, results of UL-94 tests showed that if MMP alone is added into PLA, 20 percent is the minimum amount to keep V_0 grade. When 15 percent or less MMP of the total amount added in PLA, the drips can make the cottons combustion. Therefore, if we can find another additive which can help getting rid of the drips may achieve V_0 grade. We found that organically MMTs are useful in preventing dripping. So during the research, we mixed PLA/MMP system with C-20A. Only 1 percent C-20A can stop the drips, UL-94 result certified that 84 percent of PLA blend with 15 percent of MMP and 1 percent of C-20A matched V_0 grade. That is to say only 16 percent of additives added into PLA can help improve flame retardant, a great advance when compared to those addition agents which more than 20 percent need to mix with PLA to pass V_0 . But if more C-20A added in the system, it is hardly to extinguish in 10 seconds, since C-20A itself is not a good IFR. When considering RDP coated MMP, MMP-RDP, it has familiar phenomenon as MMP when mixed with PLA. The mixture of 80 percent PLA and 20 percent MMP-RDP can reach V_0 even if it will drip when combustion, the drips cannot ignite the cotton. However, when the amount of MMP-RDP reduced to 15%, the drips can ignite the cotton. Which shows it will not work better than MMP alone.

Ce-RDP system is another considerable IFR and we are working on it nowadays. Both cellulose and RDP are biodegradable materials, so they can easily degrade under the temperature of burning. This makes the PLA/Ce-RDP mixture more likely to drip when carrying on UL-94 tests. As they are considered to be degraded during combustion and will take away a lot of heat, they can help the specimen to extinguish quickly. However, as RDP is a liquid and cellulose is also liable to degrade, the specimen will keep dripping when burning. And dripping so fast will make the cotton combustion. We tried to blend C-20A or C-30B in the system to prevent the drips or slow the drips, but the results demonstrated that when organically MMTs mixed in PLA/Ce-

RDP system, the extinguish time will be much longer and the material cannot slake in 10 seconds, which will lead to V₂ grade or even NG.

Recently, we searched more literatures and discovered that MoS₂ can work on polymer retardant. Z. Matusinovic et al documented MoS₂ is helpful to enhance the thermal stability of polystyrene (PS) and Poly (methyl methacrylate) [19]. K Zhou et al published that the peak heat release rate (pHRR) of PVA/MoS₂ nanocomposite decreased when compared to pure PVA [20]. Therefore, we are trying to use this inorganic nanotube as an additive to enhance PLA retardant. The current results showed that 15 percent of MoS₂ and 85 percent PLA mixture can reach V₀. Further study is needed to figure out whether we can reduce the amount of MoS₂.

3.2 Results and discussion of clays, HNTs, GNPs and MoS₂ polymer nanocomposites

3.2.1 Microstructure of nanocomposites

In order to detect the dispersion of clays, nanotubes, GNPs and MoS₂ in polymer, the specimens and the nanotube layers were imaged with SEM (figure 9a-i).

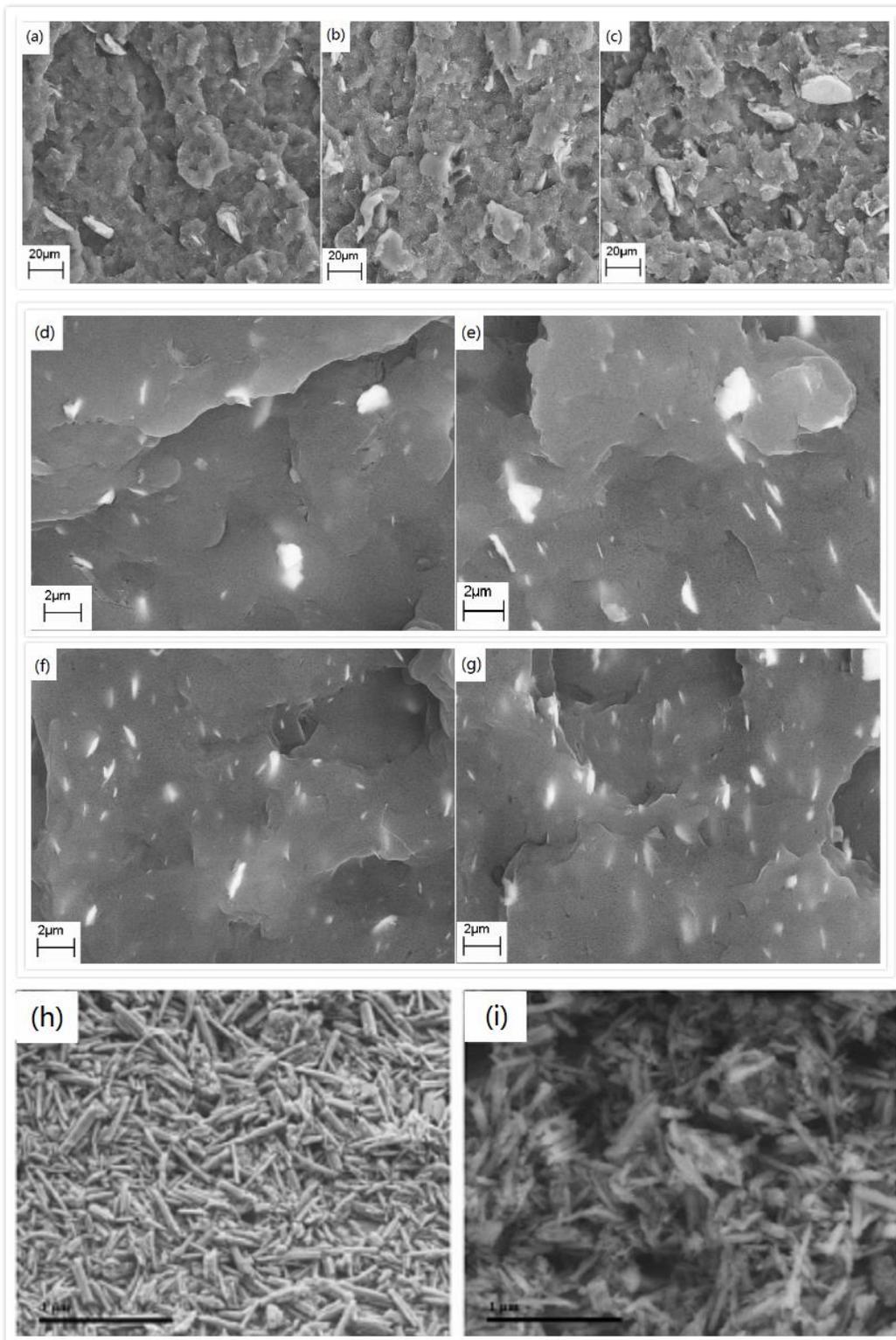


Figure 9. SEM image of nanocomposites: (a) 100HDPE2C-RDP, (b) 100HDPE4C-RDP, (c) 100HDPE6C-RDP, (d) 100PP2MoS₂, (e) 100PP4MoS₂, (f) 100PP6MoS₂, (g) 100PP6MoS₂, (h) HNTs, (i) H-RDP.

From the images, we can get the information that, for HDPE/C-RDP system, the scale was picked as 20 micron meters, while for PP/MoS₂ system, the scale was picked as 2 micron meters. Because when C-RDP mixed with HDPE, it is more likely to gather together and form larger clay barriers. The larger clay groups means less dispersion in HDPE. According to Figure 9a-c, it seems that 4 percent of C-RDP is the best exfoliated in HDPE when compared to 2 percent and 6 percent. Both 6 percent and 2 percent C-RDP have large clay groups shown in the SEM images, which will lead to a decrease in the mechanical properties and we will discuss later. It is obvious that most of MoS₂ can disperse well in PP when analyzing Figure 9d-g. As the scale is 2 micron meters, which means the barriers are small and they will not gather together. When more MoS₂ mixed with PP, we will see a better dispersion and most of the barriers trend to regular distribution. That is to say the barrier size kept at a same level and the direction of the barriers most point in the same direction. In contrast to C-RDP exfoliate in HDPE, the MoS₂ barriers form elongated shape. The specific value of length over the width is an important element to influence the gas diffusion. The better exfoliation helps to maintain the mechanical properties and also helps to form a series of barriers which can reduce the gas diffusion.

3.2.2 Mechanical Properties

3.2.2.1 Tensile properties of polymer/clay nanocomposites

The Young's modulus results of HDPE/clay, LDPE/clay and PP/MoS₂ nanocomposites are listed in Table 7-9, and they are plotted in Figure 10-12, respectively.

Table 7. Young's modulus results of HDPE/clay nanocomposites

Sample	Young's Modulus (GPa)	Sample	Young's Modulus (GPa)
HDPE	1.49	HDPE	1.49
HDPECNa+2	1.33	HDPEC20A2	1.47
HDPECNa+4	1.54	HDPEC20A4	1.60
HDPECNa+6	1.66	HDPEC20A6	1.44
HDPE	1.49	HDPE	1.49
HDPECRDP2	1.37	HDPEG2	1.47
HDPECRDP4	1.77	HDPEG4	1.48
HDPECRDP6	1.85	HDPEG6	1.47

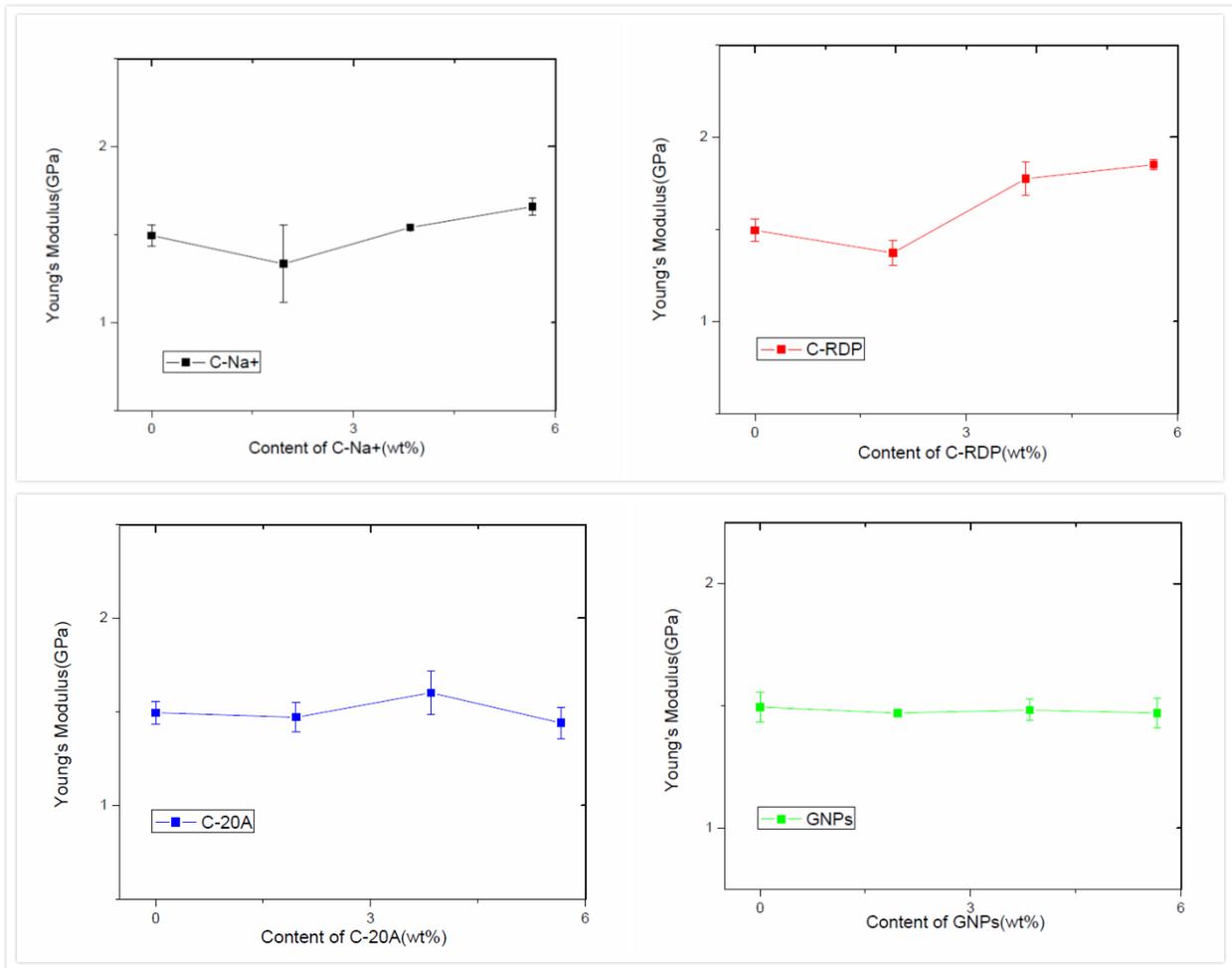


Figure 10. Young's Modulus of HDPE/clay nanocomposites

Table 8. Young's Modulus results of LDPE/clay nanocomposites

Sample	Young's Modulus (GPa)	Sample	Young's Modulus (GPa)
LDPE	0.30	LDPE	0.30
LDPECNa+1	0.32	LDPEC20A1	0.16
LDPECNa+3	0.33	LDPEC20A3	0.21
LDPECNa+5	0.38	LDPEC20A5	0.20
LDPE	0.30	LDPE	0.30
LDPECRDP1	0.26	LDPEG1	0.32
LDPECRDP3	0.27	LDPEG3	0.34
LDPECRDP5	0.36	LDPEG5	0.34

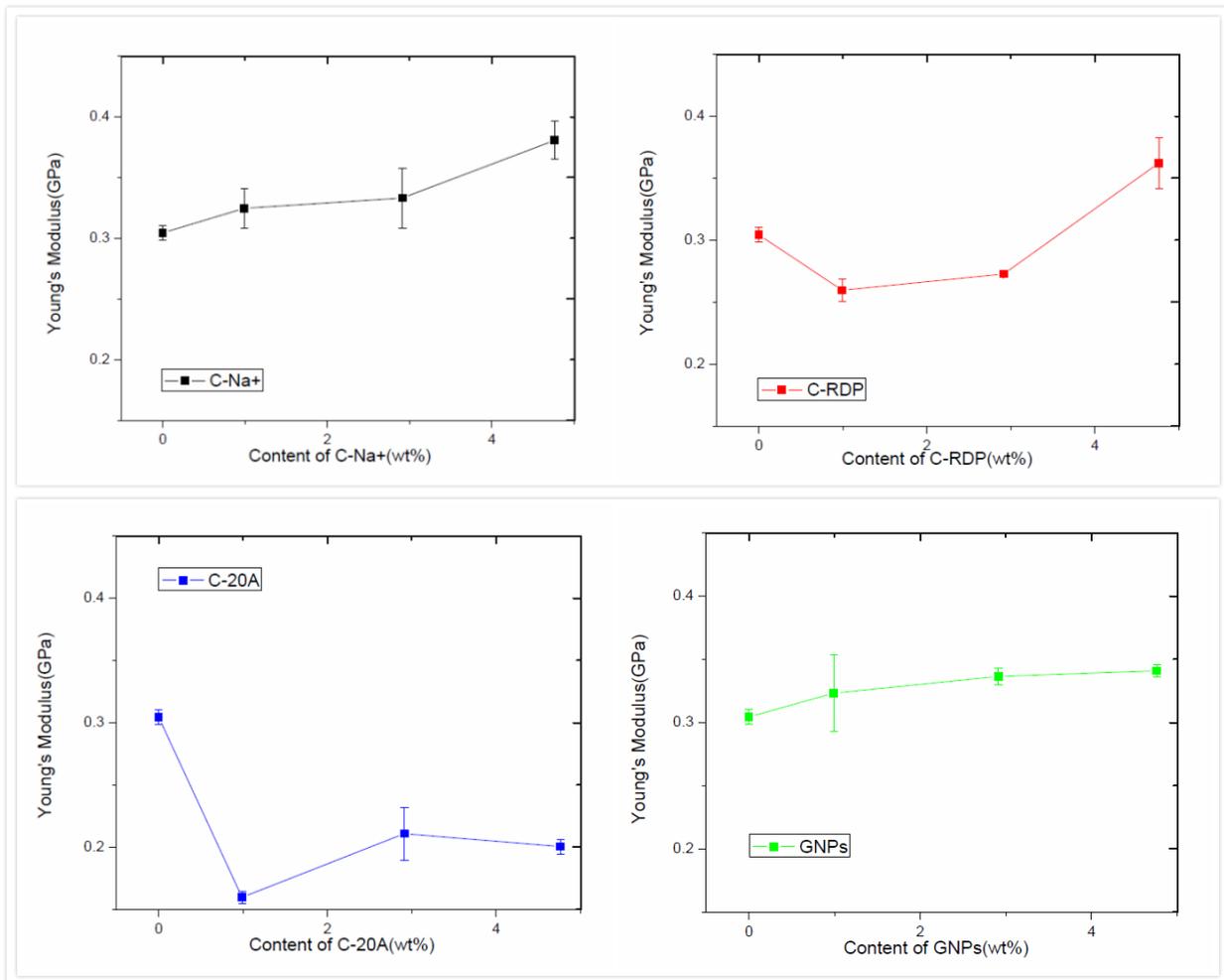


Figure 11. Young's Modulus of LDPE/clay nanocomposites

Table 9. Young's Modulus results of PP/MoS₂ nanocomposites

Sample	Young's Modulus (GPa)
PP	1.61
PPMoS ₂ 2	2.14
PPMoS ₂ 4	2.30
PPMoS ₂ 6	2.32
PPMoS ₂ 8	2.38

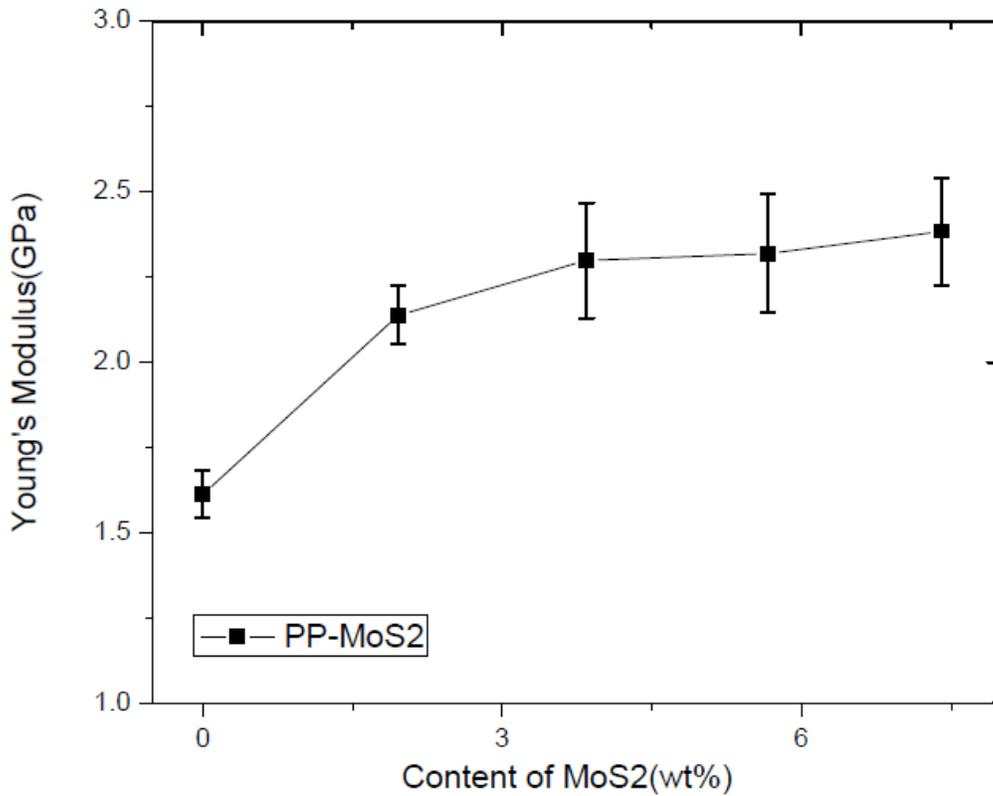


Figure 12. Young's Modulus of PP/MoS₂ nanocomposites

This series of results show a lot information about the enhancement and weaken of the Young's modulus. For each sample, we tested several specimens to get the average and calculated the error. When referring to Table 7 and Fig. 10, we listed all the groups of HDPE/clay nanocomposites with the nanoparticle content of 0,2,4,6 of HDPE. Young's modulus of pure HDPE is 1.4933 GPa. According to the results of these four groups, C-Na⁺ and C-RDP mixed

HDPE nanocomposites have a weaker modulus when the clays at a lower concentration. However, with the increase in clay content, the modulus is gradually reinforced. While C-20A and GNPs failed to enhance the modulus. This is understandable because different kinds of clays will have different exfoliation situations in HDPE matrix. When comparing HDPE/C-Na⁺ and HDPE/C-RDP systems, the results shows that C-RDP is better than C-Na⁺ to strengthen the modulus at each clay content. Therefore, the largest reinforcement of the modulus is achieved by C-RDP, which certifies RDP coated C-Na⁺ is well dispersed in HDPE and C-RDP is the most efficient clay to reinforce HDPE. This is also shown in Fig. 10. We can see from the images that, they are not trend to have linear increase or decrease with the increase of clay weight fraction. However, when increasing the content of C-Na⁺ and C-RDP, they are able to effectively enhance the Young's modulus.

Similar to HDPE, we did four series of study on LDPE. As the same with HDPE/C-20A, this clay also failed to enhance the modulus of LDPE. C-Na⁺ and C-RDP still succeeded to reinforce the modulus of LDPE. But GNPs had a quite different performance on HDPE and LDPE. In the last image of Fig. 11, the modulus is slightly increased, which means even though GNPs is no better than C-Na⁺ and C-RDP, it can enhance the modulus of LDPE. The most important is, unlike C-Na⁺ and C-RDP, which are not able to reinforce the modulus at lower content, lower content of GNPs can also enhance the modulus. Hence, if we need to maintain the modulus with lower amount of clays, GNPs is considerable to be a good choice.

Finally, when referring to PP, it is obvious that MoS₂ can effectively reinforce the modulus of PP. With higher MoS₂ content, we observed higher modulus. This proved that when the content of MoS₂ increased from 0 to 8 percent of PP, the exfoliation of MoS₂ in PP will be better, which

is also confirmed by the SEM images of PP/MoS₂. From Fig. 9d-g, the images demonstrated that with higher content of MoS₂, better and more regular dispersion occurred.

The tensile tests can list the degree of elongation and tensile strength as well. The degree of elongation is a reflection of the degree of “flow” of the sample when shear stress is applied [21]. The elongation results and tensile strength of HDPE/clay, LDPE/clay and PP/MoS₂ nanocomposites are listed in Table 10-12, and they are plotted in Figure 13-18, respectively.

Table 10. Elongation results and tensile strength of HDPE/clay nanocomposites

Sample	Elongation (%)	Tensile Strength (MPa)	Sample	Elongation (%)	Tensile Strength (MPa)
HDPE	14.79	16.91	HDPE	14.79	16.91
HDPECNa⁺2	11.79	16.80	HDPEC20A2	10.29	11.94
HDPECNa⁺4	10.53	16.84	HDPEC20A4	9.24	14.66
HDPECNa⁺6	10.48	15.51	HDPEC20A6	10.00	13.64
HDPE	14.79	16.91	HDPE	14.79	16.91
HDPECRDP2	11.73	15.34	HDPEG2	9.72	14.48
HDPECRDP4	10.64	15.67	HDPEG4	9.78	13.92
HDPECRDP6	10.27	16.77	HDPEG6	9.90	13.59

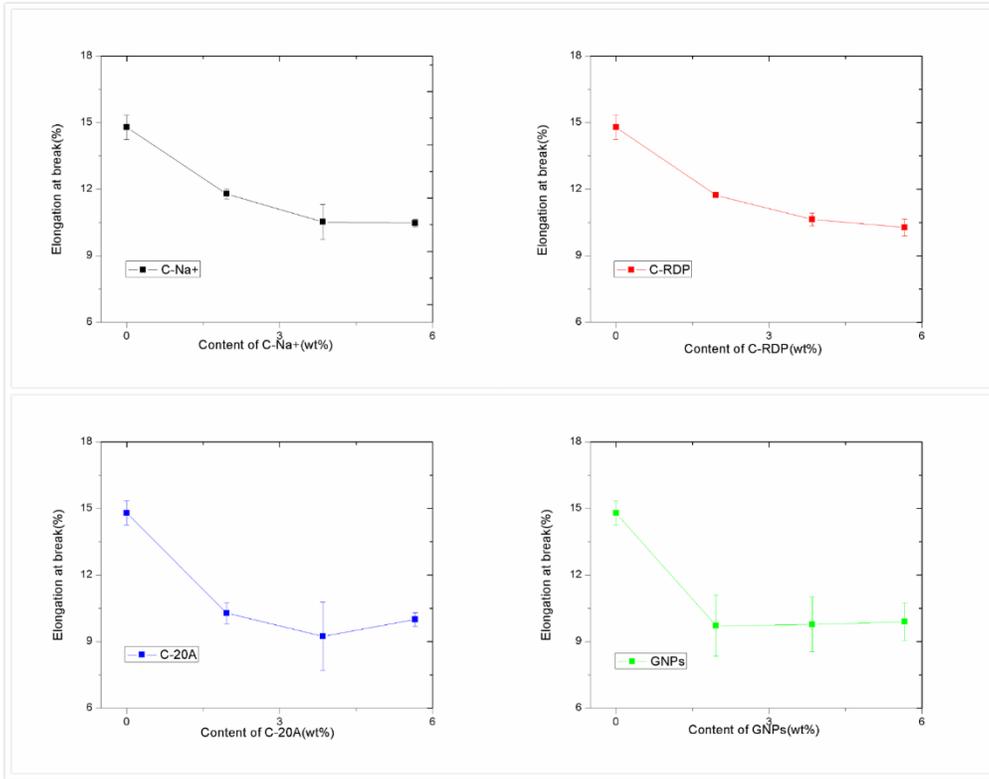


Figure 13. Elongation at break of HDPE/clay nanocomposites

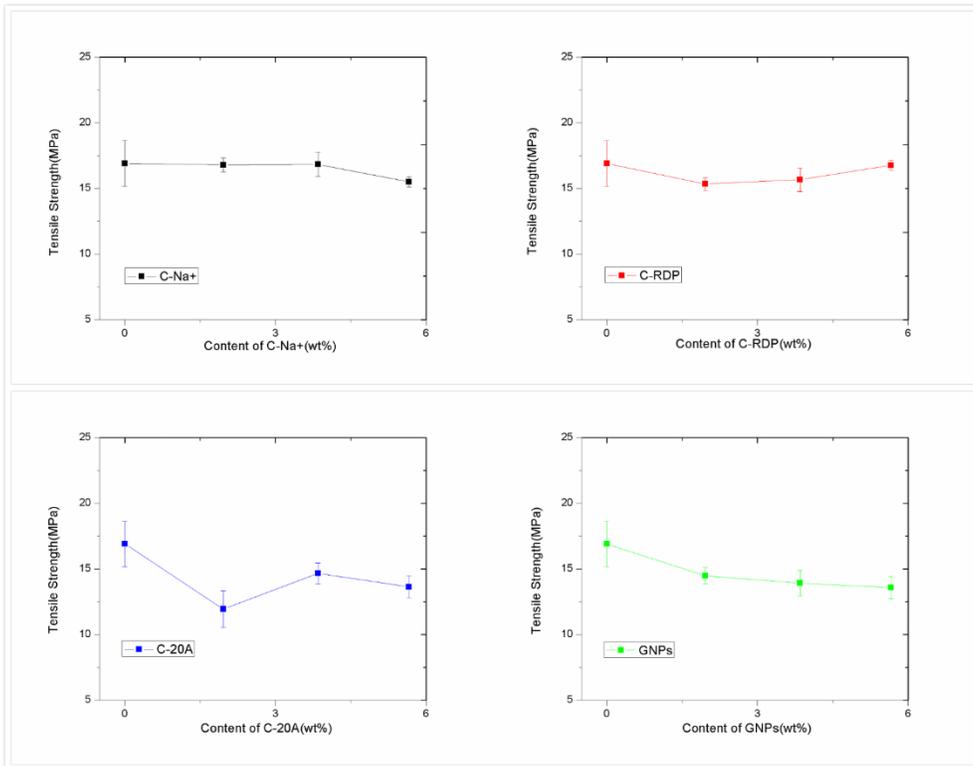


Figure 14. Tensile strength of HDPE/clay nanocomposites

Table 11. Elongation results and tensile strength of LDPE/clay nanocomposites

Sample	Elongation (%)	Tensile Strength (MPa)	Sample	Elongation (%)	Tensile Strength (MPa)
LDPE	82.55	7.48	LDPE	82.55	7.48
LDPECNa ⁺ 2	77.32	7.41	LDPEC20A2	81.01	5.89
LDPECNa ⁺ 4	66.63	6.43	LDPEC20A4	87.03	6.03
LDPECNa ⁺ 6	63.36	7.10	LDPEC20A6	77.61	5.73
LDPE	82.55	7.48	LDPE	82.55	7.48
LDPECRDP2	77.91	6.61	LDPEG2	73.24	6.86
LDPECRDP4	79.26	6.80	LDPEG4	63.69	7.11
LDPECRDP6	72.94	7.23	LDPEG6	63.88	7.21

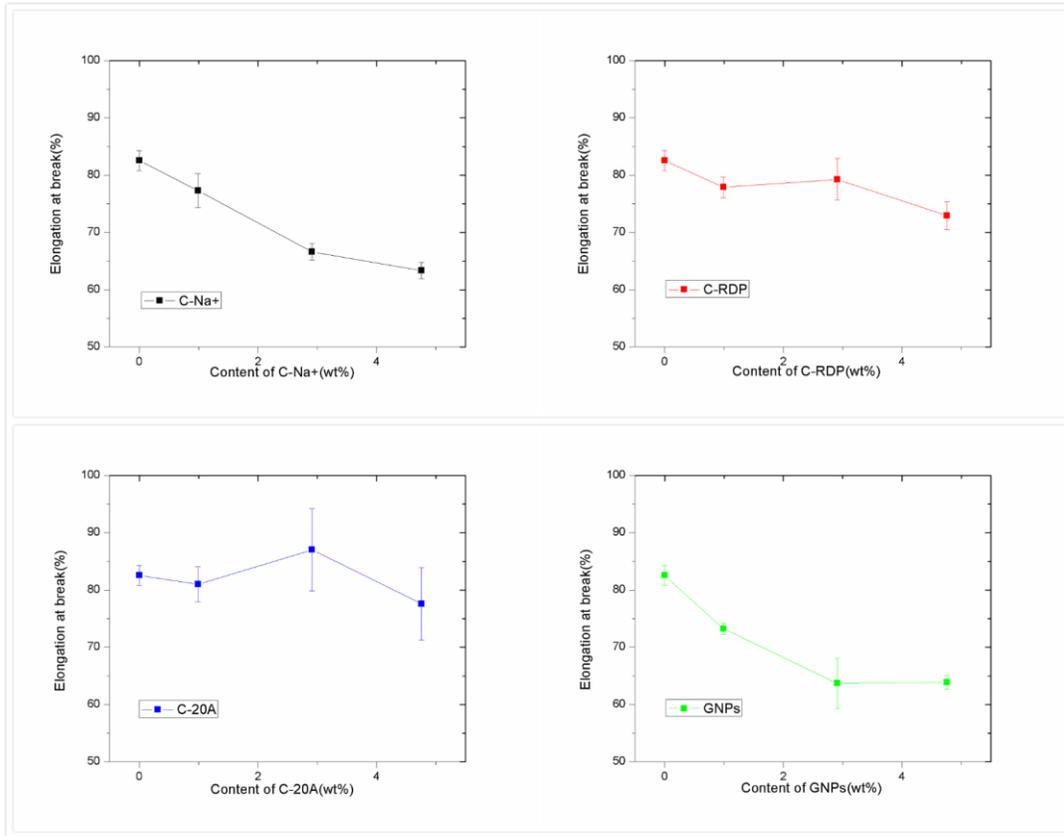


Figure 15. Elongation at break of LDPE/clay nanocomposites

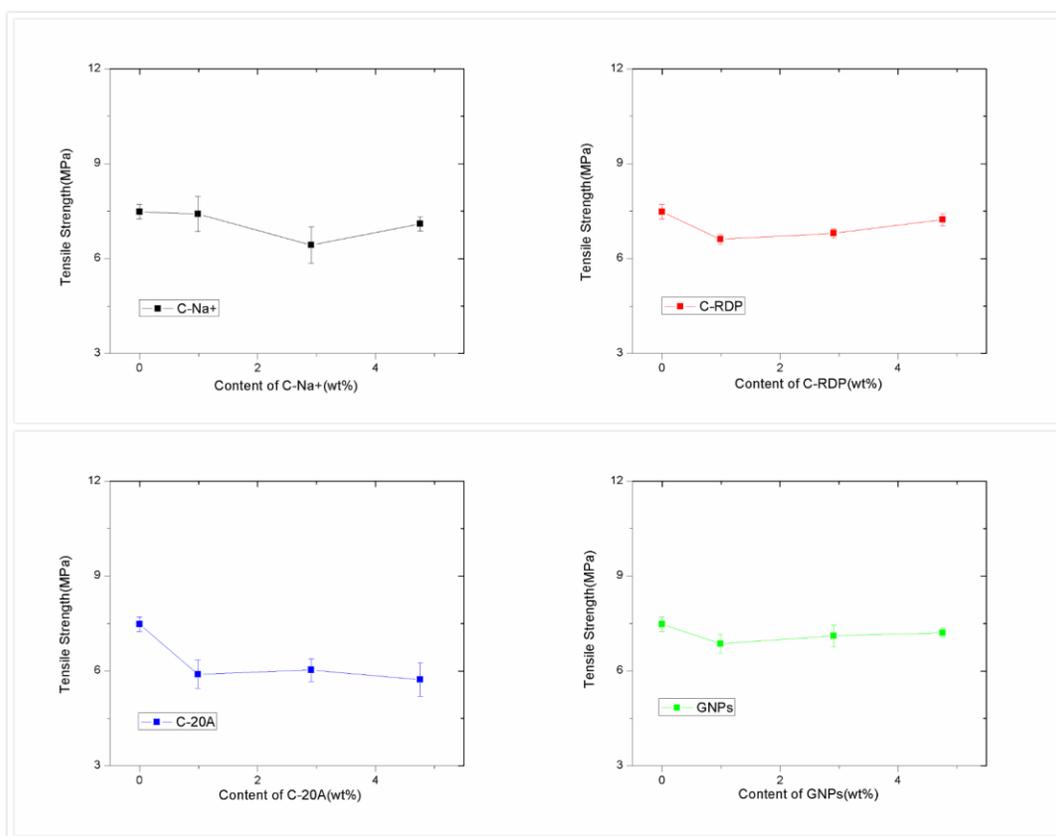


Figure 16. Tensile strength of LDPE/clay nanocomposites

Table 12. Elongation results and tensile strength of PP/MoS₂ nanocomposites

Sample	Elongation (%)	Tensile Strength (MPa)
PP	6.44	18.37
PPMoS ₂ 2	5.04	22.55
PPMoS ₂ 4	5.00	24.67
PPMoS ₂ 6	4.99	24.88
PPMoS ₂ 8	4.86	26.18

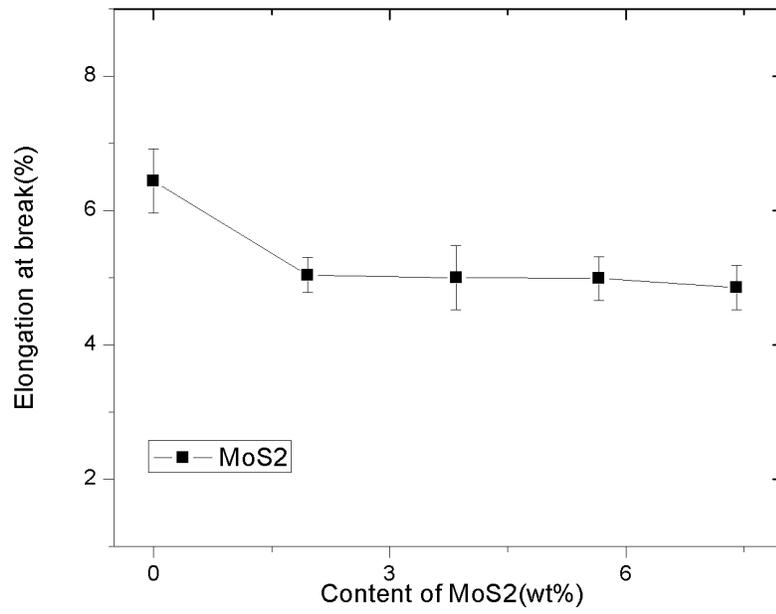


Figure 17. Elongation at break of PP/MoS₂ nanocomposites

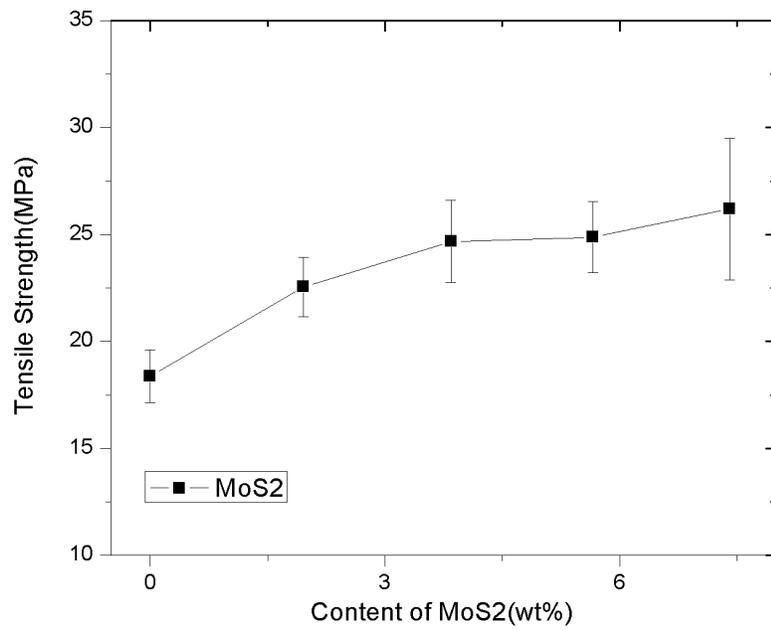


Figure 18. Tensile strength of PP/MoS₂ nanocomposites

In contrast to the modulus, the degree of elongation shows a different trend of all the specimens. For all contents of HDPE/clay nanoparticles, the elongations are decreased. The most proper reason is that when nanoparticles mixed in the polymer, strong adsorption of the polymer chains occurs on the filler interfaces so it will restrict their motion under stress. The result is, the chains are more likely to rupture rather than flow, which makes the samples more brittle and the elongation of the samples will decrease. When it turns to the tensile strength, compared to pure HDPE, the samples' tensile strength is decreasing with the increasing of clay contents, which illustrates that even though C-Na⁺ and C-RDP can help enhancing the modulus of HDPE, they embrittled HDPE and they are not sufficient enough to reinforce HDPE.

For LDPE/clay specimens, they are similar to the HDPE nanocomposites when considering the elongation at break. The degree of elongation of LDPE nanocomposites decreases when more clays mixed with LDPE. Unlike HDPE nanocomposites, the tensile strength of LDPE/C-RDP series and LDPE/GNPs series decreased at the beginning and then increased when the content of clays increased and had the propensity of keeping the same level as pure LDPE. Therefore, for C-RDP and GNPs mixed LDPE samples, the increase of the Young's modulus counterbalanced the decrease of the elongation so they can help maintaining the tensile strength.

PP/MoS₂ nanocomposites have the best results and the plots. At first, when only 2 percent of MoS₂ blended with PP, the elongation had a huge reduce and the tensile strength had great improved. When the content of MoS₂ increased, the elongation decreased slowly and the tensile strength kept increasing. The efficient exfoliation of MoS₂ in PP makes up for the reduction of elongation, so it leads to a strength of the material at the modulus and the tensile strength.

3.2.2.2 Impact resistance of polymer/clay nanocomposites

Impact strength is the capability of the material to withstand a suddenly applied load and is expressed in terms of energy. Impact tests are used in studying the toughness of material. A material's toughness is a factor of its ability to absorb energy during plastic deformation. Brittle materials have low toughness as a result of the small amount of plastic deformation that they can endure. LDPE, which is more flexible than HDPE and PP, has a higher toughness and it will not break during Izod impact test. The results of HDPE/clay and PP/clay nanocomposites are listed in Table 13, 14 and plotted in Figure 19, 20, respectively.

Table 13. Impact strength of HDPE/clay nanocomposites

Sample	Impact Strength (J/m)	Sample	Impact Strength (J/m)
HDPE	27.74	HDPE	27.74
HDPECNa+2	20.06	HDPEC20A2	27.89
HDPECNa+4	21.09	HDPEC20A4	26.38
HDPECNa+6	22.15	HDPEC20A6	21.87
HDPE	27.74	HDPE	27.74
HDPECRDP2	26.66	HDPEG2	24.78
HDPECRDP4	27.98	HDPEG4	21.60
HDPECRDP6	27.18	HDPEG6	18.95

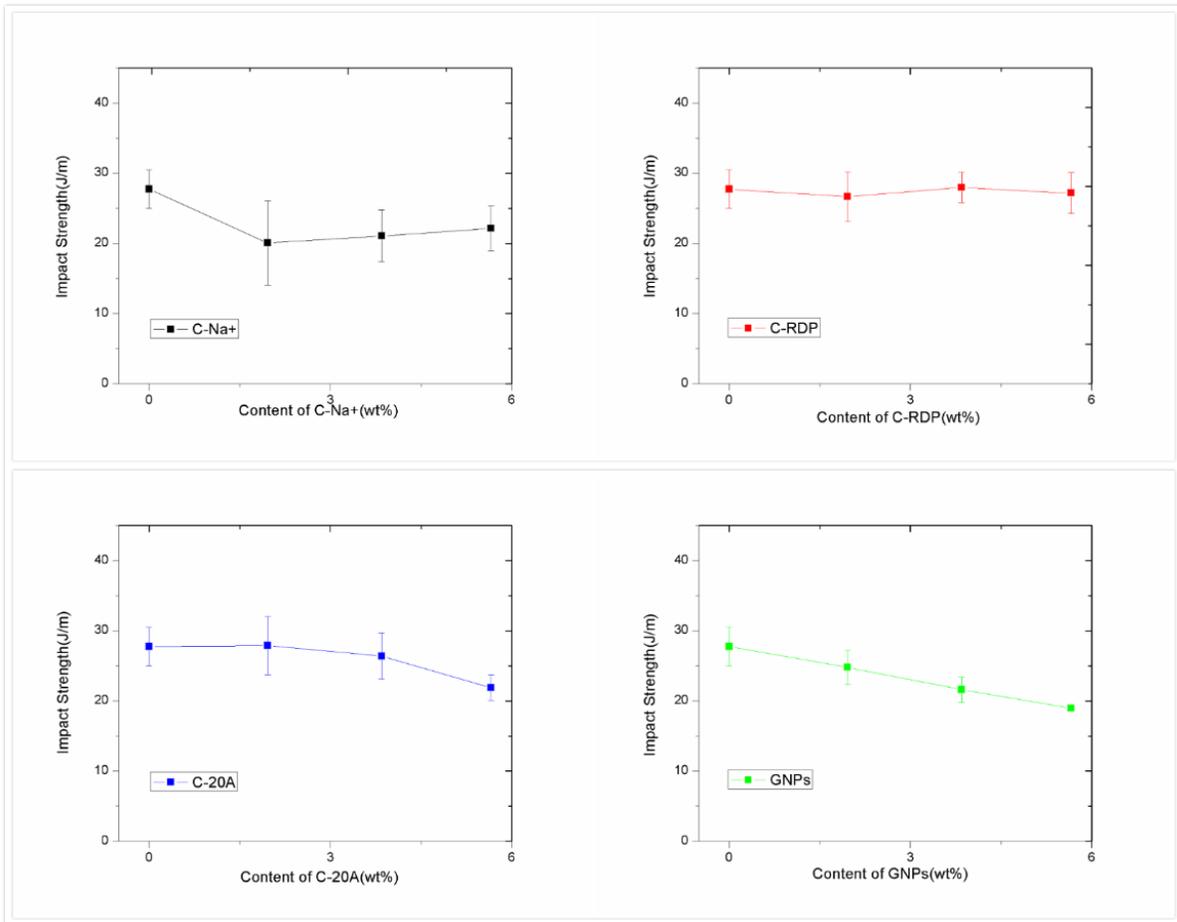


Figure 19. Impact strength of HDPE/clay nanocomposites

Table 14. Impact strength of PP/clay nanocomposites

Sample	Impact Strength (J/m)	Sample	Impact Strength (J/m)
PP	17.37	PP	17.37
PPMoS ₂ 2	17.37	PPG2	18.95
PPMoS ₂ 4	16.50	PPG4	17.89
PPMoS ₂ 6	17.37	PPG6	15.78
PPMoS ₂ 8	17.37	PPG8	17.90

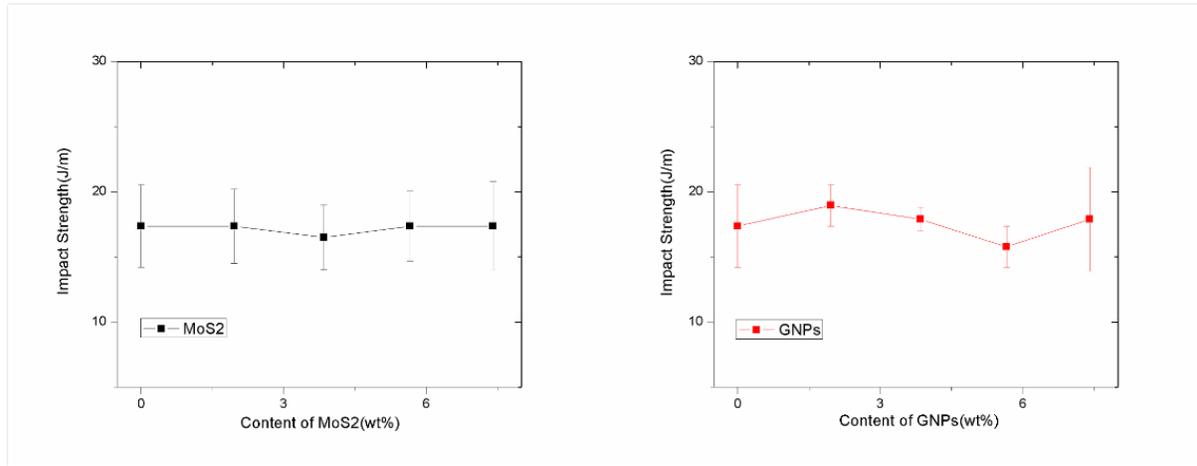


Figure 20. Impact strength of PP/clay nanocomposites

According to Fig. 16 and Table. 13, it is obviously that with the increase of C-Na⁺, C-20A and GNPs content, the impact strength reduced. Therefore, these three series of nanocomposites have a lower toughness than pure HDPE. So you can endure smaller plastic deformation when the same applied load acted on the specimens. C-Na⁺, C-20A and GNPs mixed with HDPE embrittled HDPE, only C-RDP helped to maintain the impact strength. The reason is C-RDP is better dispersed in HDPE than other clays, the distance between the clay particles are larger because they are less likely to gather together, so it is harder for them to form crack size. Moreover, when nanoparticles mixed inside the polymer matrix, they will form internal stress, which leads to the local crack formation. When an external stress σ , is applied, the stress will generate at the tips of

the particles, σ_{max} is the critical stress to break the specimen at the crack tip, and it follows the formula [22]:

$$\sigma_{max} = \sigma \left(1 + 2 \frac{a}{b} \right) \quad (3.1)$$

Where, a and b are the length and width of the particles in the matrix. According to the SEM images, we can figure out that at lower concentration of clays, the crack would be smaller than higher concentration, and higher concentration of clays showed a better exfoliation. So the number of non-exfoliated particles are smaller and the distance between the particles will be larger, which made it more difficult to form cracks.

This also happened on PP/clay nanocomposites. From the SEM image of PP/MoS₂ system, with the increasing of MoS₂ concentration, the exfoliation seems to be more regular. At lower concentrations of MoS₂, one can see many protruding clay tactoids, which resulted from the high internal stress at the tips of tactoids. On the other hand, HDPE/C-RDP nanocomposites have larger tactoids, which would cause larger interstices in polymer matrix and would weaken the structure and make it more prone to crack under stress. That's why HDPE/C-RDP will have a decrease in the impact strength. However, for PP/MoS₂ nanocomposites, the tactoids are much smaller, so the interstices in polymer matrix will be much smaller as well, which would help to maintain the impact strength.

3.2.3 Dynamic mechanical analysis

The DMA results of HDPE/C-RDP nanocomposites are plotted in Figure 21a, b, and the glass transition point (T_g) is listed in Table 15.

Table 15. Glass transition temperatures (T_g) of HDPE/C-RDP nanocomposites

Sample	T_g ($^{\circ}\text{C}$)
HDPE	-110.00
HDPECRDP2	-111.38
HDPECRDP4	-110.68
HDPECRDP6	-112.32

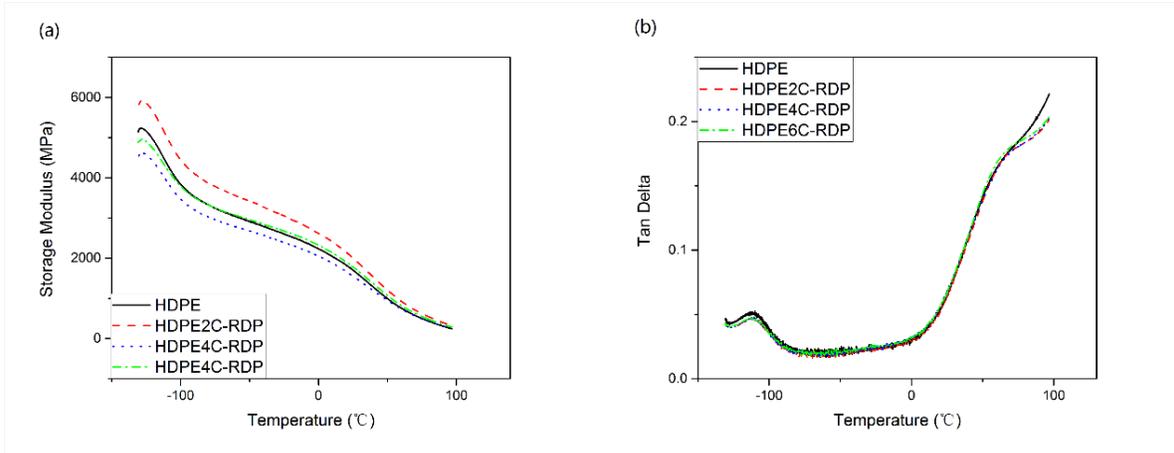


Figure 21. DMA results of HDPE/C-RDP nanocomposites: (a). Storage modulus, (b) Tan Delta

DMA is used to study the viscoelastic behaviors of polymers. An important application of DMA is to measure the glass transition temperatures of polymers, at the glass transition, the storage modulus decreases dramatically and the loss modulus reaches a maximum [23]. One can see from Table 15 that HDPECRDP2, HDPECRDP4 and HDPECRDP6 had decreased 1.3865°C , 0.6843°C and 2.3231°C of T_g , respectively. Which showed that all the HDPE/C-RDP nanocomposite has a decrease in T_g , and 4 percent C-RDP mixed HDPE is most close to pure HDPE, which is also shown in Fig. 21a. The storage modulus of HDPE/C-RDP displayed in Fig.21a, 4 percent C-RDP blend HDPE is the most similar to HDPE alone. While HDPECRDP2 has higher storage modulus and HDPECRDP6 has lower storage modulus when the temperature bellows the glass transition temperature. The results illustrated that only HDPECRDP2 had a stronger interaction between C-RDP and HDPE, HDPECRDP4 and HDPECRDP6 had weaker interaction between C-RDP and

HDPE. Therefore, at low concentration of clays, the rigid nanoparticles worked on the polymer enhanced the storage modulus. When higher contents of C-RDP add into HDPE, the exfoliation of C-RDP is not as good as lower concentration and we can see from the SEM image that in HDPECRDP6 image, the larger tactoids will weaken the matrix. And the SEM images showed the best exfoliation of these sample occurred in HDPECRDP4. Therefore, the impact strength of HDPECRDP4 is most similar to HDPE, which represents the endurance of sample matrix when loading a certain applied energy.

3.2.4 Differential scanning calorimetry

The DSC results of HDPE/C-RDP series and PP/MoS₂ series are plotted in Figure 22, 23 and the calculated crystallinity and melting points are listed in Table 16, 17, respectively.

Table 16. Crystallinity and melting temperature of HDPE/C-RDP nanocomposites

Sample	Crystallinity (%)	T _m (°C)
HDPE	59.81	129.07
HDPECRDP2	62.32	130.14
HDPECRDP4	59.64	129.17
HDPECRDP6	60.77	131.85

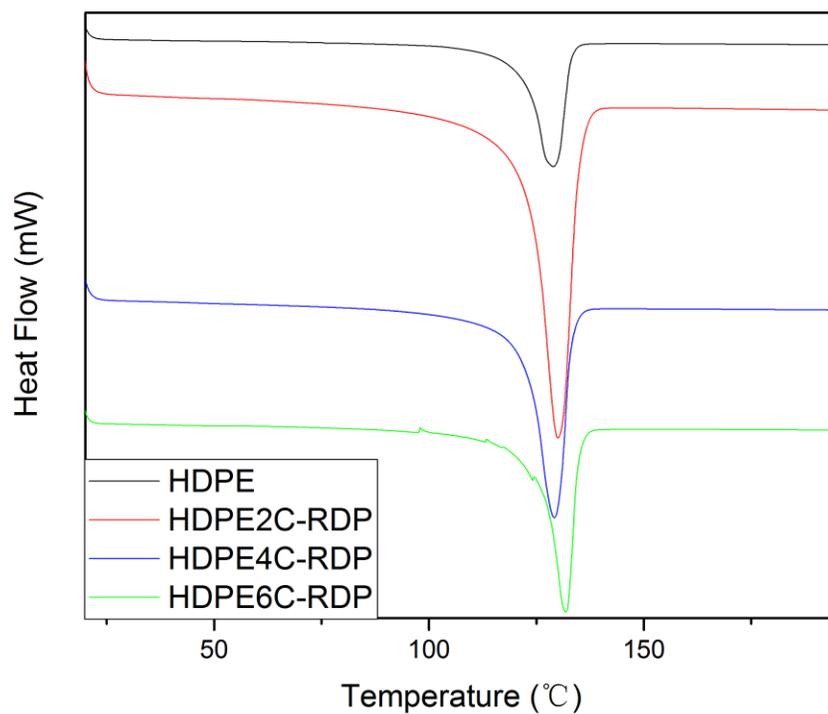


Figure 22. DSC results of HDPE/C-RDP nanocomposites

Table 17. Crystallinity and melting temperature of PP/MoS₂ nanocomposites

Sample	Crystallinity (%)	T _m (°C)
PP	45.47	165.46
PPMoS ₂ 2	49.79	164.59
PPMoS ₂ 4	50.29	165.19
PPMoS ₂ 6	50.65	165.44
PPMoS ₂ 8	50.95	166.77

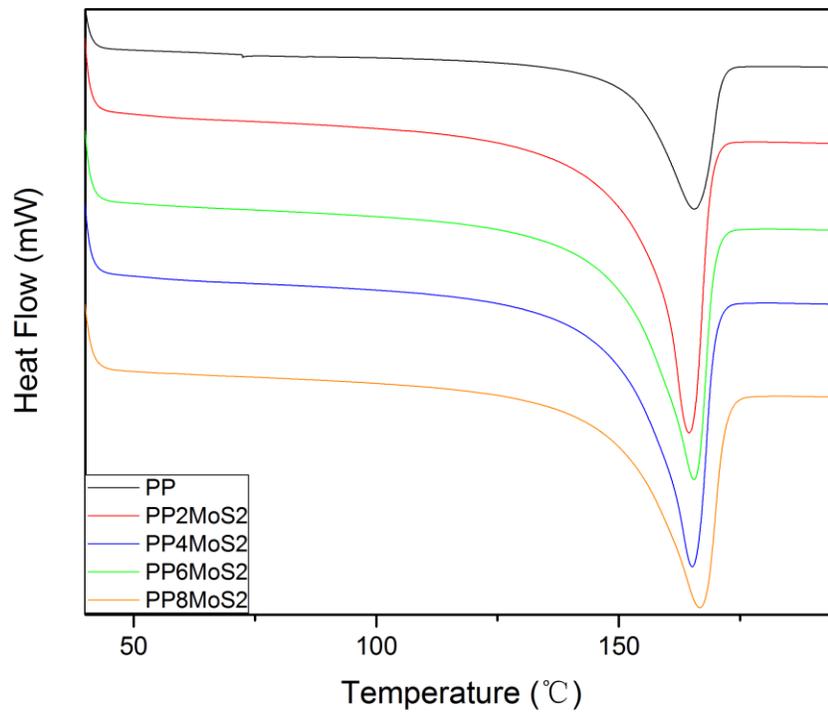


Figure 23. DSC results of PP/MoS₂ nanocomposites

HDPE and PP are both semicrystalline polymers. Addition energy is released upon melting these polymers. Differential scanning calorimetry (DSC) can be used to measure this energy. When this energy compared with the fusion of ideal fully crystallized polymers, one can get the degree of crystallinity [24, 25]. As the temperature increases, the sample reaches its melting temperature

(T_m). The melting process results in an endothermic peak in the DSC curve. Through this peak and curve, one can pick out the melting point of polymers [26].

According to Table 16, the crystallinity of HDPECRDP2 and HDPECRDP4 increased when compared to genuine HDPE, while crystallinity of HDPECRDP4 kept at almost the same level as HDPE. Higher crystallinity embrittles the material, so the mechanical properties is a little weaker than HDPE but HDPECRDP4 can maintain the strong mechanical properties as HDPE. The melting temperature of HDPE/C-RDP specimens migrated to a higher degree with the increasing crystallinity, but not a huge change. Therefore, thermal properties of HDPE preserved when C-RDP added in the system.

When discussing PP/MoS₂ system, the degree of crystallinity increased with the increasing clay content. However, the melting point showed a decrease at lower clay contents, but it was increasing with the increased content of MoS₂. Similar to HDPE, the melting point didn't change a lot. And the thermal properties maintained when MoS₂ blended with PP. Furthermore, crystallinity of PP/MoS₂ nanocomposites increased slowly from 2 percent of MoS₂ to 8 percent of MoS₂, the stable results of crystallinity also illustrated the stable impact resistance.

3.2.5 Oxygen gas permeability

It has been documented via multiple groups that by layered silicates proved to be effectively form the barriers in order to increase the route of the diffusion pathway when oxygen diffused through the matrix [27-29]. In this research, the theoretical basis is the Nielsen model, formula (3.2), which assumes the platelets of nanoparticles inside the matrix will make longer path for the gas molecules to diffuse through the polymer [30]. The platelets of nanoparticles was supposed to

be rectangular platelets with the width of L and thickness of W and they were assumed to lay perpendicular to the gas diffusion path, which lead to the longest pathway for gas to diffuse. The ideal diffusion pathway is shown in Figure 24.

$$\frac{K_{composite}}{K_{matrix}} = \frac{1-\phi}{1+\frac{\alpha}{2}\phi} \quad (3.2)$$

Where, $K_{composite}$ and K_{matrix} are the gas permeability of polymer/clay nanocomposites and pure polymers, ϕ is the volume fraction of nanoparticles and $\alpha = L/W$ is the aspect ratio of the platelets.

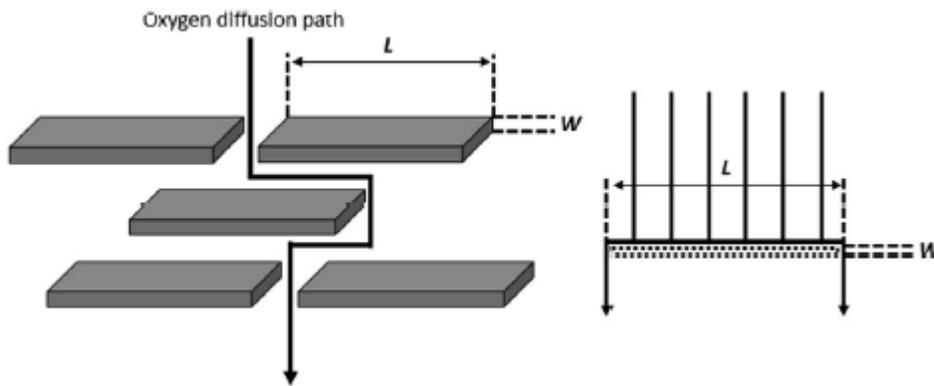


Figure 24. Ideal layered platelets and the oxygen diffusion pathway

The diffusion path of nanotubes is a bit different but quite similar to clay platelets. As the structure of nanotubes is cylindrical, when oxygen go through nanotubes, it would diffuse around the surface of the nanotubes, as shown in Figure 25.

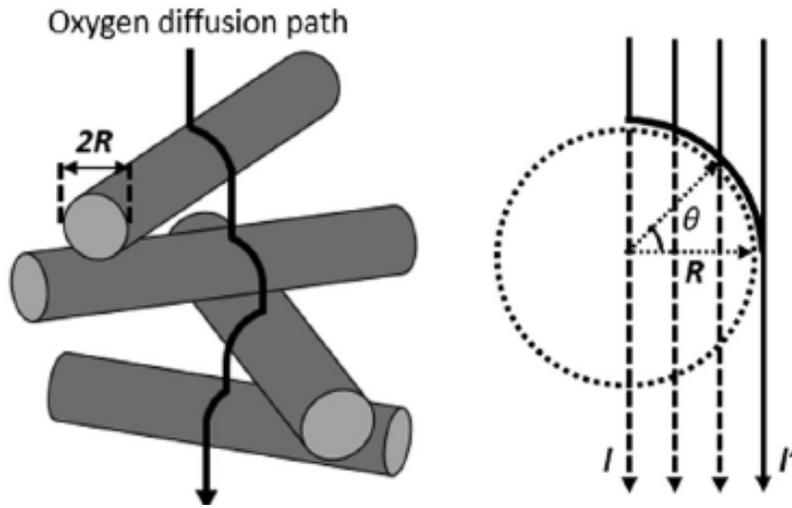


Figure 25. Ideal oxygen diffusion pathway of nanotubes

Since the structure of nanotubes is no longer rectangular like clay platelets, a modified version of Nielson model had to be developed. Y. Guo et al has documented about the oxygen permeability equation of nanocomposites with tubular additives [21]. Formula (3.3) is to calculate the model of oxygen diffusion through nanotube mixed polymers.

$$\frac{K_{composite}}{K_{matrix}} = \frac{1-\phi}{1+\frac{\pi^2-8}{16}\phi} \quad (3.3)$$

Different polymer/clay nanocomposites were studied during the research. All the results of polymer/clay nanocomposites are plotted in separate images in Figure 26a-e. Due to the difference between the density of clay, nanotubes, graphene and MoS₂, they showed different degree of volume fraction.

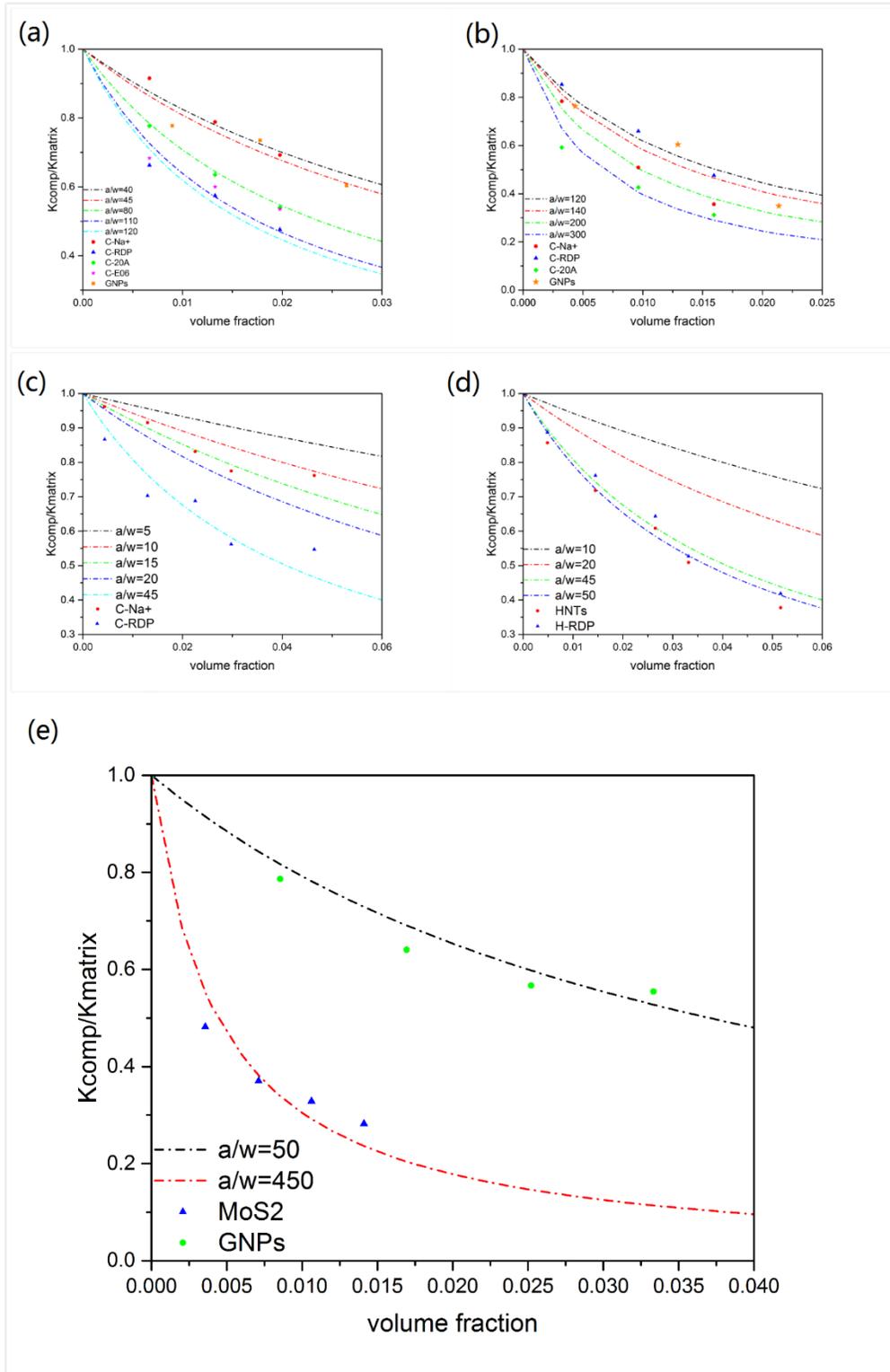


Figure 26. Oxygen permeability of nanocomposites with different volume fraction of clays. The dash-dot lines represents the fitting results of polymer nanocomposites according to the Nielsen model. (a) HDPE/clay, (b) LDPE/clay, (c) PLA/clay, (d) PLA/nanotubes, (e) PP/clay.

According to Fig. 26, when nanoparticles worked on the polymers, they can form either clay platelets or cylindrical nanotubes, which can effectively help reducing the oxygen diffusion rate through the materials. Different nanoparticles have different effect on different polymers.

In Fig. 26a, the effects of clays worked on HDPE, one can see that C-RDP and C-E06 are the most effective two clays to lower the oxygen permeability, while C-Na⁺ and GNPs are less useful to work on HDPE. This is understandable that the monolayer structure of graphene can hardly form platelets in the polymers since it is more likely for the polymers to lay on the surface of the graphite layer. And from all the discussion about the mechanical and thermal properties about the HDPE/clay nanocomposites above, C-RDP has a better exfoliation on HDPE than C-Na⁺ and C-20A, which means the better dispersion of C-RDP may have more regular directions of the clay platelets and they are less likely to form tactoids than C-Na⁺ or C-20A. As the SEM image showed, most of C-RDP had a uniform dispersion on HDPE, so they are the most effective additives to reduce the oxygen diffusion. E-06 is the improvement of RDP, it is more hydrophilic than RDP, but for other properties, these to liquids are quite similar. The C-RDP platelets in HDPE had an α about 120, which means the length of C-RDP platelets is about 120 times of its thickness.

It makes sense that GNPs would not work well on LDPE and PP as well. When referring to Fig 26b, which represents the oxygen diffusion of LDPE/clay nanocomposites, C-RDP kept the same size of platelets as exfoliated in HDPE. However, it is no better than C-20A or C-Na⁺, C-20A platelets in LDPE was with the ratio of length and thickness as high as 300. They are more efficient to prevent the oxygen diffusion through LDPE. In the future, further analysis of LDPE/clay nanocomposites will be needed to certify this.

Considering the oxygen diffusion on PLA nanocomposites plotted in Fig. 26c,d, C-Na⁺ had only a little effect on PLA, while C-RDP, HNTs and H-RDP seems to be more efficient. However, C-RDP was not as good to work on PLA as they worked on HDPE or LDPE. There is no significant difference between HNTs and H-RDP, since RDP is a liquid material, when coated on HNTs, the cylindrical nanotube size would not change a lot.

We can see a huge difference between the oxygen diffusion through PP/MoS₂ and PP/GNPs. As mentioned above, due to its layered structure, GNPs was not able to effectively form the rectangular platelets structure like clay platelets. Therefore, it acted a limited role when considering the gas diffusion. Unlike GNPs, MoS₂ is much better in decreasing the oxygen diffusion rate on PP. From Fig. 9d-g, the SEM images of PP/MoS₂ nanocomposites, most of MoS₂ formed long and thin rectangular platelets in PP, and the direction of MoS₂ platelets is a regular distribution. Therefore, matched with the mechanical and thermal properties of PP/MoS₂, they also played a significant role in terms of reducing the permeability. To further study the dimension of MoS₂ in PP, TEM tests will be held in the recent future.

Chapter 4 Conclusion

To expand the application of polymers, flame retardant is a significant issue. Different kinds of additives have been proved to be effective on PLA flame retardant. In the study, we achieved several formulas of PLA nanocomposites which can successfully pass the V_0 grade of UL-94 flame retardant test. The lowest ratio of clay contents to add in PLA and can achieve UL-94 V_0 grade is 84 percent of PLA blend with 15 percent of MMP and 1 percent C-20A. Since the contents of additives are less than 20 percent of the total quality of the samples, they can be regarded as an improvement of the former research on PLA retardant area. Recently, we are working on PLA/Ce-RDP system and PLA/MoS₂ system, and we have already made some progress. In the future, further study will take to confirm a most efficient way of PLA flame retardant. Moreover, we will do the mechanical and thermal tests to carry out further research and seek wider application.

MMT clays and their modified products are a wide range of additives to be used in many aspects. One of the applications is to enhance the properties of polymers. GNPs and MoS₂, they are both dark colored powders with significant use in materials. During the research, with lots of analysis on the mechanical and thermal properties of polymer nanocomposites, our purpose is to get some particles which can well exfoliate in polymers to reinforce the properties of polymers and to reduce the oxygen diffusion at the same time. RDP coated C-Na⁺ had a better dispersion than C-Na⁺, C-20A and GNPs when blend with HDPE. It helped to improve the degree of crystallinity of HDPE and the mechanical properties maintained. The exfoliated barriers parameter, α , was as high as 120-140, which certified an series of efficient clay platelets were formed the resulted in the reduction in oxygen permeability. In this research, according to Nielsen model, we built the ideal oxygen diffusion pathway of both clay platelets and nanotubes, and demonstrated the work with the help of SEM and TEM images. MoS₂ was supposed to be a proper additive to

PP matrix. The exfoliation of MoS₂ in PP showed as a regulation distribution in the polymer matrix. The parameter of MoS₂ platelets obtained through gas permeability reach to 450. That means elongated rectangular platelets formed. The impact strength of PP/MoS₂ maintained with the increasing MoS₂ content, while the Young's modulus, tensile strength and crystallinity was improved. Compared with MoS₂, GNPs are less effective both in enhancing the mechanical properties and reducing the gas permeability on PP. In the future, TEM images, DMA and rheology tests will be needed to further confirm the size of MoS₂ platelets and the effects of it worked on PP.

References

- [1] "SPI Resin Identification Code - Guide to Correct Use". *SPI: The Plastics Industry Trade Association*. *SPI: The Plastics Industry Trade Association*. Retrieved 21 January 2016.
- [2] Baeurle SA, Hotta A, Gusev AA (2006). "On the glassy state of multiphase and pure polymer materials". *Polymer* 47: 6243–6253.
- [3] Maier, Clive; Calafut, Teresa (1998). *Polypropylene: the definitive user's guide and databook*. William Andrew. p. 14. ISBN 978-1-884207-58-7.
- [4] S. Pavlidou, C.D. Papaspyrides, "A review on polymer-layered silicate nanocomposites". *Progress in Polymer Science*, Volume 33, Issue 12, December 2008, Pages 1119–1198.
- [5] Michael Alexandre, Philippe Dubois, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials". *Materials Science and Engineering: R: Reports*, Volume 28, Issues 1–2, 15 June 2000, Pages 1–63.
- [6] Tzong-Ming Wu, Cheng-Yang Wu, "Biodegradable poly (lactic acid)/chitosan-modified montmorillonite nanocomposites: Preparation and characterization". *Polymer Degradation and Stability*, Volume 91, Issue 9, September 2006, Pages 2198–2204.
- [7] S. Pack, T. Kashiwagi, C. Cao, C.S. Korach, M. Lewin, M.H. Rafailovich, *Macromolecules* 43 (2010) 5338-5351.
- [8] "Scientific Background on the Nobel Prize in Physics 2010, GRAPHENE" . The Royal Swedish Academy of Science.
- [9] T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme & L. C. Brinson. Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotechnology* 3, 327 - 331 (2008).
- [10] Zvonimir Matusinovic, Ruchi Shukla, E. Manias, Charles G. Hogshead, Charles A. Wilkie, Polystyrene/molybdenum disulfide and poly(methyl methacrylate)/molybdenum disulfide nanocomposites with enhanced thermal stability, *Polymer Degradation and Stability* 97 (2012) 2481-2486.
- [11] Xiaming Feng, Bibo Wang, Xin Wang, Panyue Wen, Wei Cai, Yuan Hu, Kim Meow Liew, Molybdenum disulfide nanosheets as barrier enhancing nanofillers in thermal decomposition of polypropylene composites, *Chemical Engineering Journal* 295 (2016) 278–287.
- [12] Vandersall HL. Intumescent coating systems, their development and chemistry. *J Fire Flammability* 1971; 2 (2): 97-140.
- [13] Shahab Jahromi, Wouter Gabriëlse, Ad Braam. Effect of melamine polyphosphate on thermal degradation of polyamides: a combined X-ray diffraction and solid-state NMR study.

Polymer 44 (2003) 25–37.

[14] Rafael Auras, Loong-Tak Lim, Susan E. M. Selke, Hideto Tsuji (ed.). Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications. doi:10.1002/9780470649848. ISBN 9780470293669.

[15] Nazre, A.; Lin, S. (1994). Harvey, J. Paul; Games, Robert F., eds. Theoretical Strength Comparison of Bioabsorbable (PLLA) Plates and Conventional Stainless Steel and Titanium Plates Used in Internal Fracture Fixation. p. 53. ISBN 0-8031-1897-X.

[16] "Bioengineers succeed in producing plastic without the use of fossil fuels". Physorg.com. Retrieved 2011-04-11.

[17] Xin Wang, Yuan Hu, Lei Song, Shanyong Xuan, Weiyi Xing, Zhiman Bai, Hongdian Lu. Flame Retardancy and Thermal Degradation of Intumescent Flame Retardant Poly (lactic acid)/Starch Biocomposites. *Ind. Eng. Chem. Res.* 2011, 50, 713–720.

[18] Jianxiang Feng, Shengpei Su, Jin Zhu. An intumescent flame retardant system using β -cyclodextrin as a carbon source in polylactic acid (PLA). *Polym. Adv. Technol.* 2011, 22 1115–1122.

[19] Zvonimir Matusinovic, Ruchi Shukla, E. Manias, Charles G. Hogshead, Charles A. Wilkie. Polystyrene/molybdenum disulfide and poly (methyl methacrylate)/molybdenum disulfide nanocomposites with enhanced thermal stability. *Polymer Degradation and Stability.* 97, (2012), 2481-2486.

[20] Keqing Zhou, Saihua Jiang, Chenlu Bao, Lei Song, Bibo Wang, Gang Tang, Yuan Hu, Zhou Gui. Preparation of poly (vinyl alcohol) nanocomposites with molybdenum disulfide (MoS_2): structural characteristics and markedly enhanced properties. *RSC Advances.* Issue 31, 2012.

[21] Yichen Guo, Kai Yang, Xianghao Zuo, Yuan Xue, Clement Marmorat, Ying Liu, Chung-Chueh Chang, Miriam H. Rafailovich. Effects of clay platelets and natural nanotubes on mechanical properties and gas permeability of Poly (lactic acid) nanocomposites. *Polymer* 83 (2016) 246-259.

[22] B. Cotterell, J.Y.H. Chia, K. Hbaieb, *Eng. Fract. Mech.* 74 (2007) 1054-1078.

[23] Young, R.J.; P.A. Lovell (1991). *Introduction to Polymers* (2 ed.). Nelson Thornes.

[24] GW Becker, Ludwig Bottenbruch, Rudolf Binsack, D. Braun: *Engineering Thermoplastics. Polyamides.* (in German) Hanser Verlag, 1998 ISBN 3-446-16486-3.

[25] Gottfried W. Ehrenstein, Gabriela Riedel, Pia Trawiel: *Practice of thermal analysis of plastics.* Hanser Verlag, 2003, ISBN 3-446-22340-1.

[26] Dean, John A. (1995). *The Analytical Chemistry Handbook.* New York: McGraw Hill, Inc. pp. 15.1–15.5. ISBN 0-07-016197-6.

[27] S.S. Ray, P. Maiti, M. Okamoto, K. Yamada, K. Ueda, *Nano Lett.* 2 (2002) 1093-1096.

[28] S.S. Ray, K. Yamada, M. Okamoto, Y. Fujimoto, A. Ogami, K. Ueda, *Polymer* 44 (2003) 6633-6646.

[29] G. Choudalakis, A.D. Gotsis, *Eur. Polym. J.* 45 (2009) 967-984.

[30] L.E. Nielsen, *J. Macromol. Sci. Part A* 1 (1967) 929-942.