Preparation and Properties of Na-MMT/PVA Nanocomposite Emulsion

Buqin Xu
State Key Lab of Pulp and Paper Engineering
South China University of Technology
Guangzhou, China
e-mail:164307517@qq.com

Guilong Xu*
State Key Lab of Pulp and Paper Engineering
South China University of Technology
Guangzhou, China
e-mail:feglxu@scut.edu.cn

Jin Yang
State Key Lab of Pulp and Paper Engineering
South China University of Technology
Guangzhou, China
e-mail:jjjyang135@qq.com

Jian Hu
State Key Lab of Pulp and Paper Engineering
South China University of Technology
Guangzhou, China
e-mail:640952121@qq.com

Abstract—Na-MMT/Poly-Vinyl acetate-Acrylate (PVA) nanocomposite emulsion was prepared by in situ emulsion polymerization in the presence of exfoliated Na-MMT suspension. Effect Na-MMT content on the polymerization process and stability of the emulsion was studied. The water-proofing, thermal stability and anti-aging properties of the prepared Na-MMT/PVA composite polymer films were studied by water absorption ratio, thermo-gravimetric analysis (TGA) and anti-ultraviolet aging test. The results show that stable Na-MMT/PVA nanocomposite emulsion is obtained when the Na-MMT content is lower than 2.0wt%. TEM(Transmission electron microscopy) observation indicates that the Na-MMT/PVA composite latex has a layer-sphere combined structure. The composite polymer film presents much better water-proofing, thermal stability and anti-aging properties than the pure PVA polymer film.

Keywords- Exfoliated Na-MMT; Nanocomposite emulsion; Properties ; Sturcture; Water profing

I. INTRODUCTION

Poly vinyl acetate-Acrylate copolymer emulsion is widely applied in coating and adhesive field[1,2] for its excellent film formability, adhesion performance, as well as low cost and environmental friendly. Unfortunately, vinyl acetate-acrylate latex film exhibits a bad resistance to water, heat and UV light, which limit its further application in many areas. Many methods are devoted to solve these problems, the Polymer/Layered Silicate (PLS) nanocomposite have drawn much research attention because they effectuate in improving material properties by the presence of a small amount of layered silicate, and promise superior or unique properties in comparison with those of the conventional polymer composites[2,3]. By introducing a few weight percent of clay into the polymer matrix, these nanocomposites exhibit significant increases in many properties, such as mechanical properties[4], thermal stability[5] and improved barrier properties[6,7]. Of the methods used in the preparation of Polymer/MMT nanocomposites, in situ emulsion polymerization offers the ability to impart significant control over both the polymer architecture and the final structure of the composite[8-9]. However, exfoliated Na-MMT/PVA composite emulsions and their performances were seldom studied in detail.

In this study, exfoliated Na-MMT was first prepared and the Na-MMT/PVA composite emulsion was obtained by in situ emulsion polymerization. Effect of Na-MMT content to the polymerization of the composite emulsion was studied. TEM was used to observe the micro-structure of the nanocomposite latex. The properties of the nanocomposite emulsion film were test. The results shows that the prepared Na-MMT/PVA composite emulsion presents much better water-proofing, thermo stability and anti-aging properties.

II. EXPERIMENT

Materials

Vinyl acetate(VA), Butyl acrylate(BA), N-Methylolacrylamide(N-MA) and Methacrylic acid(MAA) were purchased from Shanghai Lingfeng Chemical Co., Ltd. in China. Sodium montmorillonite(Na-MMT) was provided by Zhejiang Fenghong clay Chemicals Co., Ltd. China. Allyloxy polyoxyethylene(10)nonyl ammonium sulfate(DNS-86) was purchased from Shuangjian Co. Ltd. China. Ammonium persulfate(APS) was purchased from Guanghua Chemical Co., Ltd. in China. Water was purified by a Milli-Q system (Millipore).

Preparation of exfoliated Na-MMT suspension

The required weights of Na-MMT and distilled water were put into a beaker and stirred for 24 h at about 300rpm at room temperature. Then the mixture was subsequently treated in an ultrasonic cell disruptor for 24h. Exfoliated Na-MMT suspension was finally obtained.

Preparation of Na-MMT/PVA nanocomposite emulsion

The required weights of exfoliated Na-MMT suspension, 0.4g DNS-86 and appropriate amount of water were poured into a flask and the temperature was

raise to 60°C. Pre-emulsified monomers (20.0g VAc, 18.0g BA, 1.0g MAA, 1.0g NMA) were obtained by emulsified monomers in the mixture of 30.0g water and 0.40g DNS-86 at room temperature for about 30 min. Initiator solution was obtained by dissolved 0.6g APS in 30.0g water. When the temperature was raise to 60°C, 20wt% of the pre-emulsified monomers and 40wt% of the APS solution was added into the flask, then the temperature was raise to 75°C. After additional 30 min of equilibration time, the remaining mixed monomers and initiator were added into the flask drop-by-drop simultaneously within 2h. Then the reaction was continued at 75°C for another 2h.

Characterization

The average particle size of nanocomposite latex was measured by a Malvern particle size analyzer (ZS-Nano-S Malvern Instruments Ltd., Britain). Water absorption is defined as $(W_{bef}-W_{aft})/W_{bef}$ * 100%, where W_{bef} and W_{aft} are the weight of the latex film before and after immersion. The latex films were immersed in deionized water for 12h. TEM measurements were performed on a transmission electron microscope (TEM, Model JEM–100CXⅡ, Japan). One drop of the suspension was diluted into water and placed on a carbon-coated copper grid to be stained with 1.0wt% phosphato-tungstic acid (HPA) for 3 min and dried in air before observation. Thermo-gravimetric analysis (TGA) was performed by a Q550 TGA System (TA Instruments, USA) under the nitrogen atmosphere at a heating rate of 10°C/min from 50 to 500°C. Anti-aging test was conducted under a 30 watt ultraviolet light (Wave length 313nm) at the distance of 20cm.

III. RESULTS AND DISCUSSION

Effects of Na-MMT content on the nanocomposite emulsion

Table.1 shows the effects of Na-MMT content on the polymerization and stability of the prepared nanocomposite emulsion.

TABLE.1 Properties of Na-MMT/PVA composite emulsion

Na-MMT content (wt%)	Particle size (nm)	Monomer conversion rate (wt%)	Coagulum (wt%)	Storage stability
0	89.6	97.17	0.22	>90d
0.5	85.1	96.11	0.26	>90d
1.0	96.5	96.06	0.49	>90d
1.5	108	95.87	0.55	>90d
2.0	125	94.55	0.74	>90d
2.5	146	94.17	2.22	Sediment found in 60d
3.0	179	93.26	2.59	Sediment found in 15d

From Table.1 we can see that the particle size of the latex decrease when the Na-MMT content is lower that 1.0wt%, then the particle size of the latex increase as the Na-MMT content increase. This is due to the reason that during the emulsion polymerization process, a part of monomers polymerized around the exfoliated Na-MMT sheets and formed core-shell nanocomposite, this rendered an increase in number of emulsion particle. Therefore, the emulsion particle size decreased. However, if the content of Na-MMT exceeds the intercalative capacity of monomer, emulsion will change into the blend of in situ composite and direct composite and therefore the particle size increase[10].The monomer conversion rate decrease as the Na-MMT increase, this is because the anionic Na-MMT would neutralized with the ionic initiator, therefore lead to the inactive of part of the initiator. One can also see that the prepared nanocomposite emulsion can stay stable for 90 days when Na-MMT content is under 2.0wt%, but over dosage of Na-MMT leads to a sudden increase of coagulum and short shell life.

Effects of Na-MMT content on the Water absorption ratio

Water absorption ratio of the latex films is important parameters for characterization of water-proofing property, the tested results are shown in Figure.1.

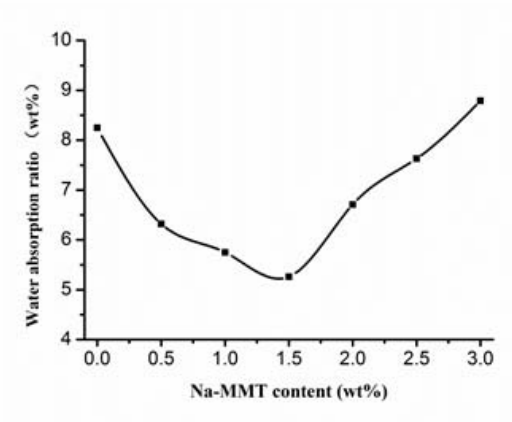

Figure1. Effect of Na-MMT content to the water absorption of the composite films

The water absorption ratio was greatly influenced by the Na-MMT content, which was due to the following two reasons: On the one hand, the large aspect ratio of the exfoliated layer-structured Na-MMT was well dispersed in the composite material and act as an obstructer in the composites, which produces a tortuous path-way and therefore makes the water molecular harder to penetrate into the composite network[11]. On the other hand, the surface of Na-MMT was full of hydrophilic group, which makes the composite material more hydrophilic and easier to absorb water.

As shown in Fig.1, with the increase of the Na-MMT content, the water absorption ratio of the latex films decreased when the Na-MMT content is lower than 1.5wt%, then the water absorption ration increase as the Na-MMT content increase. This is due to the fact that when the Na-MMT content was lower than 1.5wt%, the obstructive effect of the Na-MMT act as the dominate role and therefore effectively decrease the water absorption ratio of the composite. However, when the Na-MMT content is higher than 1.5wt%, the hydrophilicity of the Na-MMT take the more important role and leads to an increase of the water-absorption ratio of the composite film.

Micro-structure of nanocomposite latex

TEM was used to observe the micro-structure of the latex particles. Fig.2 shows the micro-structure of PVA latex and the nanocomposite latex (1.5wt Na-MMT)

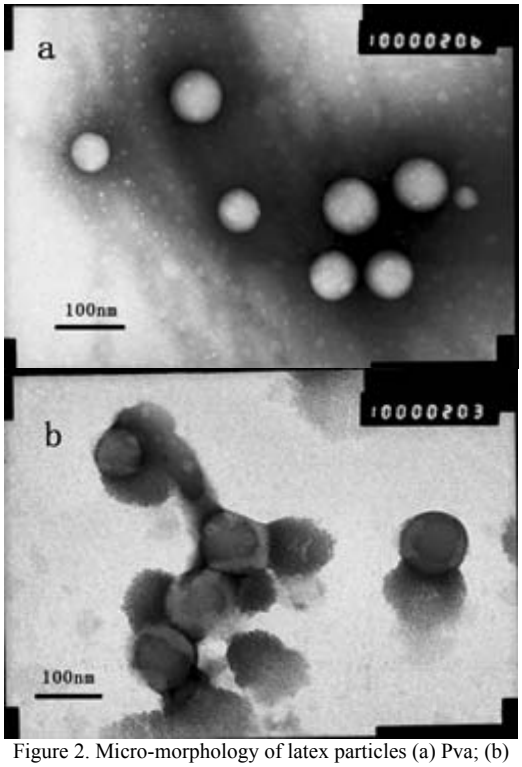

Figure 2. Micro-morphology of latex particles (a) Pva; (b) nanocomposite latex 1.5% Na-MMT

As in shown in Fig.2 (a), the PVA latex shows a sphere structure. However, in Fig.2 (b), we can see that the Na-MMT was in an exfoliated state, the composite latex shows a layer-sphere combined structure.

Thermo stability of Na-MMT/PVA nanocomposite

Effect of Na-MMT content on the thermal stability of the nanocomposite films was investigated by comparing the TGA curves of the nanocomposite material and the results are shown in Fig.3.

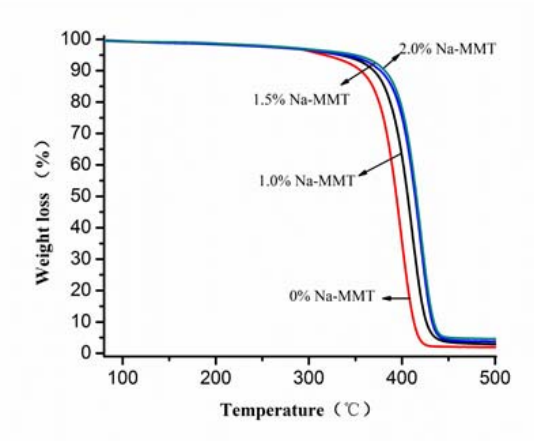

Figure 3. Effects of Na-MMT content to the thermal stability of the composite

From Fig.3 We can see that the thermal stability of the nanocomposite film improved greatly with the content of Na-MMT. The decomposition of the PVA film began at about 315°C and ended at about 420°C, whereas, the composite film with 1.5wt% Na-MMT content began to decompose at about 345°C and decomposed completely at about 440°C. Obviously, the thermal stability of the nanocomposite film is much better than the pure PVA polymer. The enhancement of thermo-oxidative stability of nanocomposites is due to the reason that The clay acts as a heat barrier and therefore restricted thermal motion of polymer chains localized inside the clay galleries as in the case of intercalated nanocomposites[12], and thus improves the copolymers' thermal stability.

Effects of Na-MMT content on anti-aging property of composite films

The anti-aging test was conducted according to the GB/T1766-1995 test， the aging of the coatings was divided into 6 levels(from 0 to 5) according to their appearance (3 items: loss of gloss, splitting and surface tackiness), level 0 represents barely no damage, level 5 represents worst damaged. The anti-aging test results are shown in Table.2.

TABLE .2 Destruction of coatings after UV tests (720h)

Na-MMT content (wt%)	Level		
	Loss of gloss	Cracking	Surface tackiness
0	3	3	4
0.5	3	2	3
1.0	2	2	2
1.5	2	1	1
2.0	2	1	1

When the polymer film was under UV light, the polymer chain was easy to degrade in to small polymer chain and therefore damage the performances of the polymer film. From Table.2 we can see that the anti-aging property of Na-MMT/PVA composite coating is obvious better than the PVA coating. The pure PVA film was severe damaged after the UV aging test. However, introducing a few Na-MMT into the PVA system can great enhance the anti-UV properties of the polymer film. This is due to the fact that the large aspect ratio of the exfoliated layer-structured Na-MMT can effectively play as a shield for the composite coating and reflects the UV light, therefore increasing the anti-aging properties of the composite films.

IV. CONCLUSION

Na-MMT/PVA nanocomposite emulsion was prepared in the presence of exfoliated Na-MMT suspension by in situ emulsion polymerization. Stable nanocomposite emulsion is obtained when the Na-MMT content is lower than 2.0wt%. TEM observation result shows that the nanocomposite latex was a layer-sphere structure. The composite coating shows better water-proofing, thermo stability and anti-aging properties than that of the pure PVA polymer film. It's expected that the large-scale production of Na-MMT/PVA nanocomposite emulsion will enable practical industrial applications.

ACKNOWLEDGMENT

The authors are grateful for the financial support from the Fundamental Research Funds for the Central Universities (Project No. 2015ZM030, 2014ZZ0075) and Students' Research Program (SRP) of South China University of Technology.

REFERENCES

[1] Naghash H J. Akhtarian R, Iravani M, Synthsis and properties of polyvinyl acetate emulsion copolymers by three novel non-ionic functional polyurethane surfactants[J]. Korean Journal of Chemical Engineering, 2014, 31(7):1281-1287

[2] Kaboorani A, Riedl B, Effects of adding nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive[J]. Composites Part a-Applied Science and Manufacturing, 2011, 42, (8):1031–1039

[3] Khan U, May P, Porwal H, et al. Improved Adhesive Strength and Toughness of Polyvinyl Acetate Glue on Addition of Small Quantities of Graphene[J]. Applied Materials and Interfaces, 2013, 5(4):1423–1428

[4] Wang Z, Pinnavaia T, Hybrid Organic-Inorganic Nanocomposites: Exfoliation of Magadiite Nanolayers in an Elastomeric Epoxy Polymer[J]. Chemistry of Materials,1998, 10(7):1820-1826

[5] Cui HW, Du GB, Development of an Exfoliated Nanocomposite Prepared by Vinyl Acetate and Organic Montmorillonite: Structure, Dynamic Mechanical Properties and Thermal Degradation[J]. Composite Interfaces, 2011, 18(7):557-573

[6] Chien AT, Lin KF, Morphology and permeability of exfoliated PVAc-MMT nanocomposite films cast from soap-free emulsion-polymerized latices[J]. Journal of Polymer Science Part A: Polymer Chemistry, 2007, 45 (23): 5583–5589

[7] Messersmith PB, Giannelis EP, Synthesis and barrier properties of poly(ε-caprolactone)-layered silicate nanocomposites[J]. J Polym Sci, Part A: Polym Chem. 1995, 33(7):1047-1057

[8] Yu YH, Lin CY, Yeh JM, et al. Preparation and properties of poly(vinyl alcohol)-clay nanocomposite materials. Polymer, 2003, 44 (12), 3553–3560

[9] Carrera MC, Erdmann E and Destéfanis HA, Preparation of poly(vinyl alcohol)/organoclay nanocomposites by casting and in situ polymerization. 15th European conference on composite materials. Venice, Italy, (2012)

[10] Feng XP, Zhong AY and Chen DB, Preparation and properties of poly(silicone-co-acrylate)- montmorillonite nanocomposite emulsion. Journal of Applied Polymer Science.2006, 101(6):3963–3970

[11] Almasi H, Ghanbarzadeh B and Entezami AA, Physicochemical properties of starch–CMC–nanoclay biodegradable films[J]. Biological Macromolecules 2009, 46(1):1–5

[12] Yılmaz O, Cheaburu CN, Gülümser G, et al. On the stability and properties of the polyacrylate/Na-MMT nanocomposite obtained by seeded emulsion polymerization[J]. European Polymer Journal. 2012, 48 (10):1683–1695