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Preparation and characterization of self-emulsified waterborne nitrocellulose

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ABSTRACT

Waterborne nitrocellulose (WNC) dispersion was successfully synthesized by self emulsification and reaction among isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) and nitrocellulose (NC). The WNC was characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy and thermal gravimetric analysis (TGA), etc. The WNC dispersion has *Z*-average particle size of 133 nm approximately and distribution index of 0.152. It is indicated by TEM that the cured WNC particles show a core–shell structure, in which hydrophobic component is encapsulated by the hydrophilic carboxyl. FTIR confirms that the reactions (i.e. IPDI and NC, IPDI and DMPA) have occurred, the —NCO group of IPDI has been consumed totally and the backbone of NC is retained. TGA reveals that the cross-linked WNC film has better thermal resistance, and the water resistance measurement confirms that it has weaker water-sensitivity.

1. Introduction

In 1833, Braconnot (Franch, 1781–1885) was the first people to prepare nitrocellulose (NC). Based on the outstanding works of several scholars such as Schonbein and Abel (Worden, 1911) the NC thin film has become a widely used material in different industries such as microelectronics, coatings, purifications, leather and DNA studies (Chen et al., 2007). Polymer film formation was used to be conducted via spraying or casting of its solution on a suitable surface followed by solvent(s) vaporization. Nowadays, however, applications of organic solvents are restricted due to the environmental and economical concerns. To reduce volatile organic compound (VOC) emissions, aqueous-based resins, namely, NC dispersed in water (i.e. NC emulsion, Waterborne nitrocellulose, WNC), have attracted much attention (George, Quinlan, & Martinsville, 1989; Ahmed & Hockessin, 1992; Winchester & Charles, 1992; Javidnia et al., 2010). These products have exhibited many features related to conventional solvent-borne coatings with the advantage of presenting low viscosity at high molecular weight, very low VOC content, reduced flammability, less odor, easy application using conventional equipment, and good applicability. The materials prepared from NC aqueous dispersions can be applied in the fields of adhesives, construction, auto, packing, transportation, electronics, textiles, tape, paper, and footwear. Water borne NC lacquers are used in wood coatings due to their degradability by microorganisms, transparency, good adhesion to the substrate, good mechanical strength, fast drying rate, ease of spraying, nice pigment dispersion and compatibility with most resins and plasticizers (Lu, Xia, & Larock, 2011; Winchester & Charles, 1991).

The former researchers outline three emulsification methods for making latices such as a waterborne nitrocellulose emulsion (John, Mohamed, & John, 1979). These are sometimes referred to as "artificial latices".

(1) *Emulsification of the polymer solution*. In this method the polymer is dissolved in a volatile solvent or a mixture of solvents which are immiscible with water. The polymer solution is then dispersed, usually by some kind of mechanical means, in water in the presence of surfactants. The volatile solvent is then removed by vacuum distillation followed by concentrating the resulting dilute latex to the desired solids. This method is reported to give latices with particles of about 1 micron in diameter.
(2) *Emulsification by phase inversion*. In this method the polymer which is being emulsified is mixed with surfactant and a volatile solvent or a mixture of solvents for the polymer. Then water is added to this solution. In the early stages of water addition, a water-in-oil emulsion is formed which upon further addition of water inverts to an oil-in-water emulsion. According to the patent of Vanderhoff et al., this method calls for greater care and control than method (1) and in addition yields latex particle diameter of about 0.8–1.0 micron or larger.
(3) *Self emulsification*. This method requires polymer molecules to be chemically modified by incorporation of functional groups

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in such a way that the polymer becomes self emulsifiable in aqueous media. This method is reported to yield very small size (0.1 μm) particles. The main disadvantage of this method is reported to be the water-sensitivity of the film due to significant proportions of the functional groups of the polymer backbone.

Spontaneous emulsification is also described in some literatures as another method of making artificial latices. This method, similar to the self emulsification method described above, however, does not require the chemical modification of the polymer molecules.

Spontaneous emulsification is reported to be the result of interfacial turbulence, diffusion of one of the components from one phase to the other, and by negative interfacial tension between two phases (Becher, 1996).

Vanderhoff concludes that the first method is a preferred way of making artificial latices. Particle size is the only disadvantage they see in the process. However, a mass of the surfactants remained in the products can often reduce the performance of the film, and the volatile solvent or a mixture of solvents in the latices can also enhance the VOC content-one of the important advantages of WNC (Lu et al., 2011).

In this study, the waterborne nitrocellulose was prepared by self emulsification from aqueous medium using isophorone diisocyanate (IPDI)/NC/dimethylol propionic acid (DMPA)/triethylamine (TEA). In order to overcome the water-sensitivity of the film due to the functional groups of the polymer backbone, the cross-linking agent was added in the emulsion when which was cured. The particle size of WNC dispersion, the morphology of the cured particles, the chemical structure, the heat resistance and water resistance of the films were investigated.

2. Experimental

2.1. Materials

The commercial product NC was supplied by Sichuan Nitrocellulose Co. (Sichuan, China). IPDI, DMPA, TEA, methyl ethyl ketone (MEK), dimethylformamide (DMF), catalysts and cross-linking agent (i.e. aziridine) were all analytical grade and were purchased from Aladdin Reagent Co. (Shanghai, China). NC and DMPA were dried in a vacuum oven (100 °C) for at least 5 h. The other materials were used after dehydration with 4 A molecular sieves for one day.

2.2. Preparation of the self-emulsified WNC

Waterborne nitrocellulose was synthesized by the reaction using IPDI, NC, DMPA and TEA. DMPA was dissolved in DMF in a 4 necked round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and heat jacket. Then IPDI/MEK was added slowly under moderate stirring (300 rpm), and the mixture was allowed to react at 40 °C until the theoretical NCO content was reached. The change in the NCO value during the reaction was determined using a standard dibutylamine back-titration method (David & Staley, 1969). Upon obtaining the theoretical NCO values, the prepolymers were heated to 75 °C and a solution, i.e. NC and the catalysts dissolved in MEK, was added and stirred for 2 h while maintaining the temperature at 75 °C. Then the reaction mixture was cooled to 40 °C and TEA was added slowly and stirred for 30 min while maintaining the temperature at 40 °C. After the reaction the deionized water was added into the reaction mixture under fast stirring (500 rpm) at room temperature for 15 min. Finally the MEK was removed under vacuum to obtain the nitrocellulose dispersion in water (WNC). The in situ polymerization process for WNC is shown in Scheme 1.

2.3. Preparation of pristine and cross-linked WNC films

The pristine and 2% cross-linking agent added WNC dispersion were casted on a tinplate sheet of 8 cm × 15 cm to make films. Drying was done at 50 °C for 30 min and 60 °C for 60 min, and formed films were cured at 120 °C for 20 min. Then the cured films were put in a vacuum oven (60 °C) under 3000 Pa for 2 days to remove the condensates for ensuring cross-linking reaction. The thickness of the films obtained in this study was about 50–150 μm.

2.4. Measurement of water resistance

The water resistance was determined as follows. The WNC films were cut into 3 cm × 3 cm pieces and dried in a vacuum oven for 24 h to determine their dry weight (W_d). Then the film was immersed in distilled water for 72 h, followed by wiping off the surface water with a piece of filter paper to determine their weight (W_t). The absorbed water content was then calculated by the formula (Bai, Zhang, Dai, & Wang, 2008):

$$W(\%) = \frac{W_t - W_d}{W_d} \times 100$$

2.5. Characterization

The particle size of WNC dispersions was determined using laser-scattering equipment (Autosizer, Melvern IIC, U.K.), the sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion. Fourier transform infrared (FTIR) spectrum of both WNC samples was recorded in the range of 3900–400 cm^{-1} using FTIR spectrometer (VERTEX 70, BRUKER, Germany) by KBr pelleting technique at the resolution of 4 cm^{-1} for 32 scans. Thermal gravimetric analysis (TGA) of about 5 mg of WNC films with and without cross-linking agent was made with TGA (TGA/DSC 1, METTLER TOLEDO, Switzerland) under nitrogen atmosphere at the heating rate of 10 °C/min from 25 to 600 °C. Transmission electron microscopy (TEM) was performed on a TEM (JEM-200CX, Japan Electronics Co., Japan) operating at 120 kV. For viewing morphology, film was floated off from the mica substrates onto deionized water and collected on TEM grids.

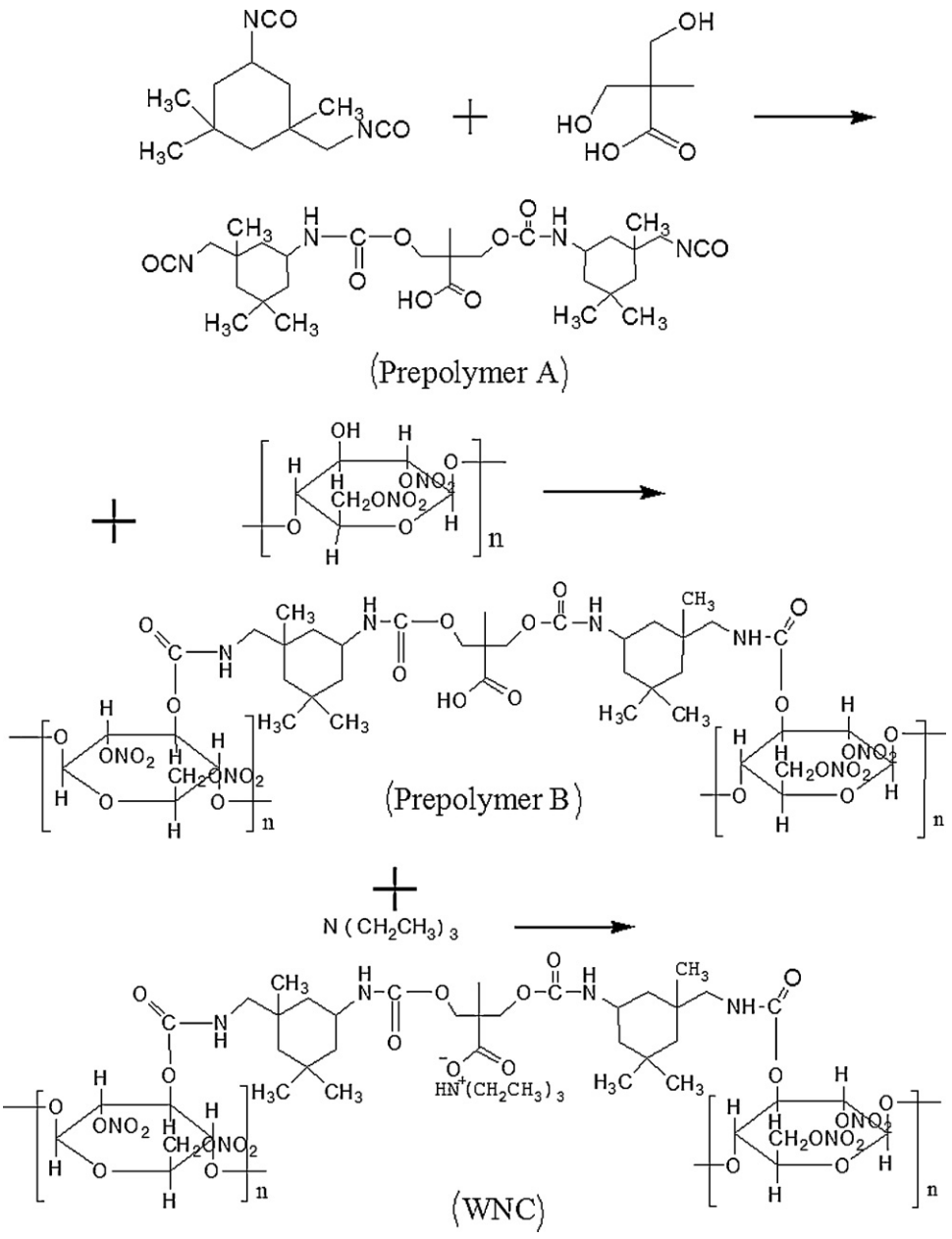
3. Results and discussion

3.1. Particle size of WNC dispersion

The particle size distribution of the WNC dispersion is shown in Fig. 1, and the solid content of the product was 36 wt%. It was found that the *Z*-average particle size of the WNC was about 133 nm (accorded with the former researches (John et al., 1979), to yield particle size about 0.1 μm by self emulsification), and its polydispersity index (PDI) was about 0.152, which is a very narrow PDI.

3.2. TEM analysis

The typical TEM images of WNC particles are shown in Fig. 2. It is found that the particles are regularly spherical with diameter of 100–200 nm and have some regular boundaries. The morphology of particles is an approximate core–shell structure, in which hydrophilic carboxyl is the shell and hydrophobic component is the core. Encapsulated by hydrophilic group, the original hydrophobic nitrocellulose is dispersed in water. The core–shell structure appears to be more visible when the particles are amplified to one hundred thousand times as shown in Fig. 2(b).



Scheme 1. Preparation of WNC.

3.3. Chemical characterization

FTIR spectra of the NC, prepolymer B (its structure is shown in Scheme 1) and WNC are shown in Fig. 3, traces a–c respectively. A typical FTIR spectrum for NC shows the —OH group stretching band at 3440.937 cm^{-1}, the $—NO_2$ group stretching vibration at 1643.3 cm^{-1}, the $—NO_2$ group bending vibration at 1274.105 cm^{-1} from trace a in Fig. 3. The peaks at 1643.3, 1274.105 and 832.58 cm^{-1} are the characteristic for NC. The three peaks at 1645.063, 1276.708 and 836.996 cm^{-1} due to the characteristic peaks of NC are prominent in trace b, which indicates the main chemical structure of NC in prepolymer B is retained. The two peaks of 1718.349 and 1546.707 cm^{-1} due to $—NH_2COO$ group indicate the —OH group of NC had reacted with the —NCO group of IPDI. The stretching band at 3440 cm^{-1} due to —OH group was weaker in trace b than in trace a, which indicates the —OH of NC was expensed by the reaction. From trace c in Fig. 3, the peaks of 647.531, 1279.436 and 841.362 cm^{-1} can be assigned to the characteristic peaks of NC. The peaks of 1714.284 and 1552.1 cm^{-1} is assigned to the urethane. The peak at 2718.626 cm^{-1} due to the carbonyl of DMPA illustrating the DMPA has taken part in the reaction. Finally, in trace c, the disappearance of the peak at 2267.989 cm^{-1} due to —NCO group indicates the reaction between DMPA and —OH group is completed. The similar FTIR results were reported for waterborne polyurethane (Gao et al., 2011; Jeon, Jang, Kim, & Kim, 2007; Kim et al., 2010; Sardon, Irusta, Fernández-Berridi, Lansalot, & Bourgeat-Lami, 2010).

3.4. Thermal gravimetric analysis

TGA results of the pristine and cross-linking agent added WNC films are shown in Fig. 4, traces a and b respectively. The temperatures of 5%, 10%, 20%, 50% and 80% weight loss are listed in Table 1. The weight loss of samples is mainly caused by the thermal decomposition of the NC. By the addition of the cross-linking agent, the WNC film displays better thermal resistance than the pristine one. To the typical samples, the 50% weight loss for WNC with and without cross-linking agent is 256.3 and 234.2 °C respectively, and there is more than 22 °C higher for the former than the

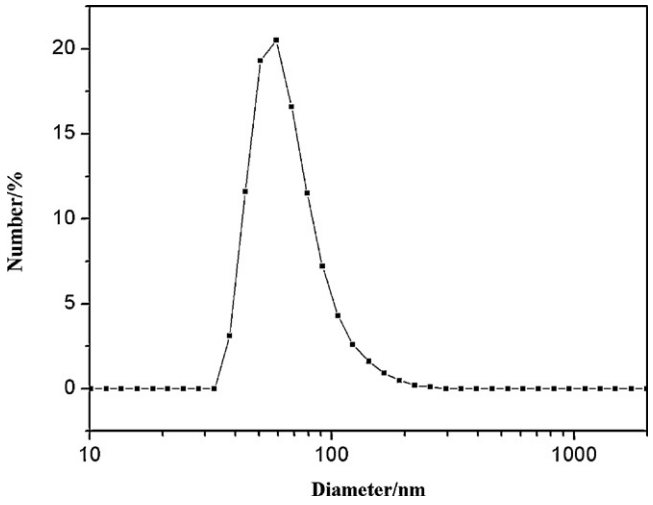


Fig. 1. Particle size distribution of WNC dispersion.

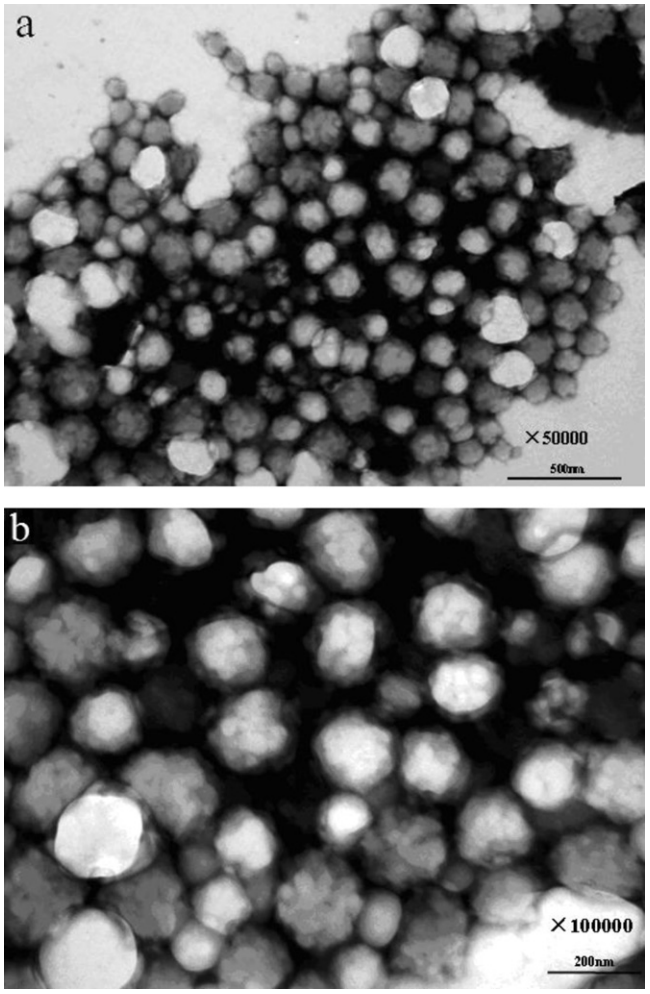


Fig. 2. TEM photographs of WNC: (a) ×50,000 and (b) ×100,000.

Table 1
TGA date of WNC films.

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	$T_{80\%}$ (°C)
a	108.5	148.0	173.8	256.3	395.2
b	105.5	131.8	156.6	234.2	362.4

Note: Sample a was the WNC film with cross-linking agent in it, and sample b was the pristine WNC film.

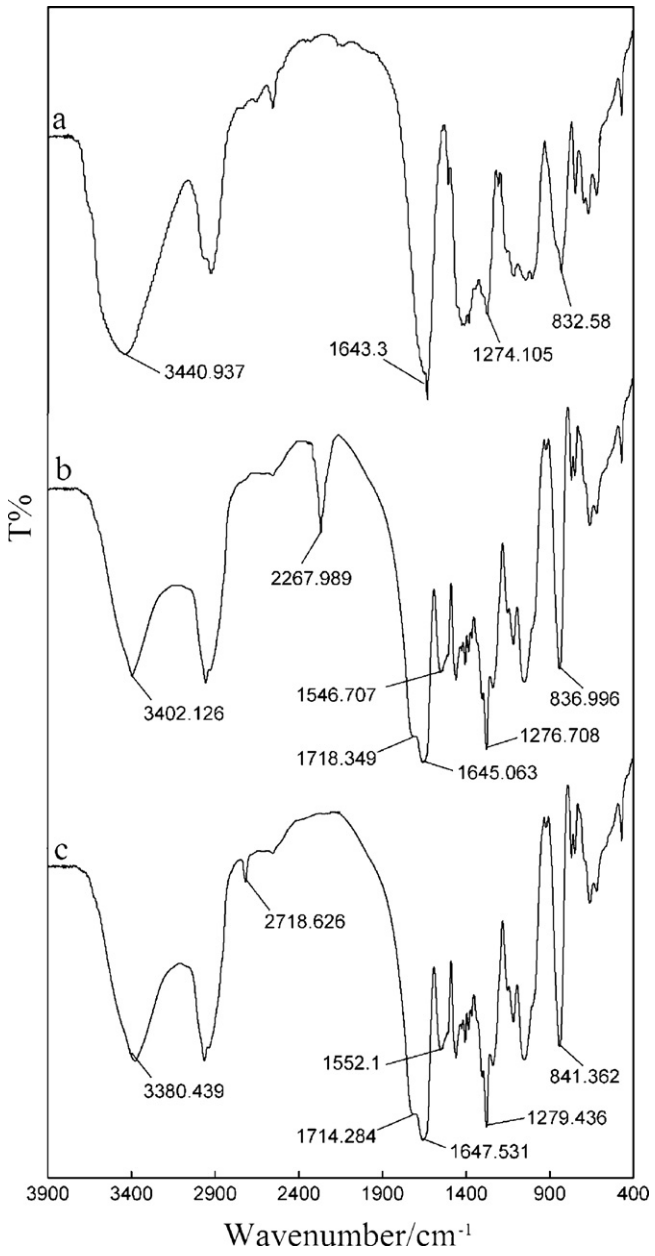


Fig. 3. FTIR spectrum of three samples, i.e. (a) NC, (b) prepolymer B, and (c) WNC.

later film. Crosslinking between chains prevents free-chain movement of polymers (Charles & Carraher, 2003), so the cross-linked WNC film shows better thermal resistance, and the better thermal resistance indicates WNC film was cross-linked effectively. The cross-linked WNC film could offer relatively greater water resistance property, which has been verified in the following section.

3.5. Water resistance

The pristine transparent buff WNC film was turned into white and opaque after it was immersed in distilled water for about 30 min, and it was gradually splitted into small pieces for about 2 h. However, the cross-linked WNC film has no apparent changes even after it was immersed in distilled water for 72 h, and the absorbed water content of which is 4.5%. The absorbed water content illustrates that the cross-linked WNC film was not sensitive to the water while the water-sensitivity is often a disadvantage of self emulsion to prepare WNC.

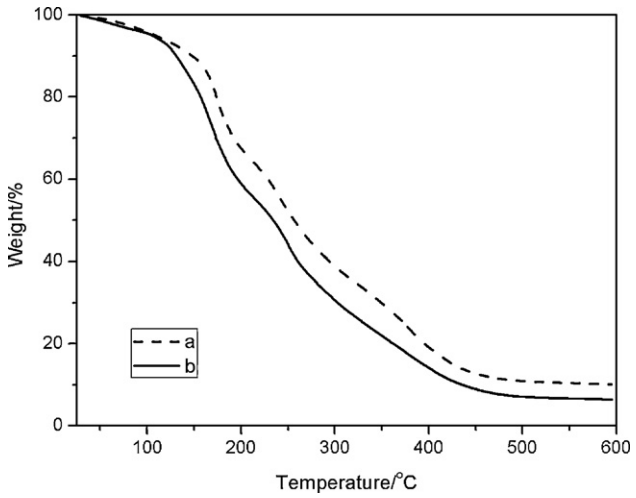


Fig. 4. TGA thermograms of WNC films, i.e. (a) with cross-linking agent addition and (b) pristine WNC film.

4. Conclusions

The self-emulsified waterborne nitrocellulose dispersion was successfully prepared by the incorporation of IPDI and DMPA into NC. The particles of WNC show uniform size of 135 nm approximately and narrow PDI of 0.18. TEM images show the regularly spherical particles display a core–shell structure, in which hydrophilic carboxyl is the shell and hydrophobic component is the core. FTIR analysis indicates that the main chemical structure of NC is retained in the WNC, and the —NCO group of IPDI has completely reacted with the DMPA. The formation of the cross-linked structure had a reinforcement effect on the thermal property and water resistance. By the addition of cross-linking agent (i.e. aziridine), the water-sensitivity of WNC film is effectively conquered.

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References

Ahmed, S. M., & Hockessin. (1992). *Process for making nitrocellulose-acrylic latices*. US Patent: 5,143,970.

Bai, C., Zhang, X., Dai, J., & Wang, J. (2008). Synthesis of UV crosslinkable waterborne siloxane–polyurethane dispersion PDMS-PEDA-PU and the properties of the films. *Journal of Coatings Technology and Research*, *5*(2), 251–257.

Becher, P. (1996). *Encyclopedia of emulsion technology* New York: Marcel Dekker Press., 281 pp.

Charles, E., & Carraher, J. (2003). *Seymour/Carraher's polymer chemistry*. New York: Marcel Dekker Press., 560 pp.

Chen, C., James Russell, W., Hong, R., Tsai, Y., Chen, C., & Tseng, K. (2007). *Process for forming nitrocellulose films*. US Patent: 7,235,307.

David, D. J., & Staley, H. B. (1969). *Analytical chemistry of polyurethanes. High polymer series* New York: Wiley Interscience Press., 45 pp.

Gao, X., Zhu, Y., Zhou, S., Gao, W., Wang, Z., & Zhou, B. (2011). Preparation and characterization of well-dispersed waterborne polyurethane/$CaCO_3$ nanocomposites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *377*(1–3), 312–317.

George, L., Quinlan, & Martinsville. (1989). *Waterborne nitrocellulose compositions*. US Patent: 4,814,015.

Javidnia, H., Mohammadi, N., Shooshtari, A. M., Ghasemirad, S., Farajpoor, T., & Ghanbari, M. R. (2010). The effect of butyl gycol acetate/ethyl acetate mixed solvents composition on nitrocellulose solution emulsification: the stability of resultant colloid and micro-filterability. *Iranian Polymer Journal*, *19*(5), 323–332.

Jeon, H. T., Jang, M. K., Kim, B. K., & Kim, K. H. (2007). Synthesis and characterizations of waterborne polyurethane–silica hybrids using sol–gel process. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *302*(1–3), 559–567.

John, W. V., Mohamed, S. E. -A., & John, U. (1979). *Polymer emulsification process*. US patent 4,177,177.

Kim, E.-H., Lee, W.-R., Myoung, S.-W., Kim, J.-P., Jung, Y.-G., Nam, Y.-S., et al. (2010). Characterization of waterborne polyurethane for ecofriendly functional floor plate. *Progress in Organic Coatings*, *67*(2), 102–106.

Lu, Y., Xia, Y., & Larock, R. C. (2011). Surfactant-free core–shell hybrid latexes from soybean oil-based waterborne polyurethanes and poly(styrene-butyl acrylate). *Progress in Organic Coatings*, *71*(4), 336–342.

Sardon, H., Irusta, L., Fernández-Berridi, M. J., Lansalot, M., & Bourgeat-Lami, E. (2010). Synthesis of room temperature self-curable waterborne hybrid polyurethanes functionalized with (3-aminopropyl)triethoxysilane (APTES). *Polymer*, *51*(22), 5051–5057.

Winchester, C., & Charles, M. (1991). Waterborne nitrocellulose wood lacquers with lower VOC. *Journal of Coatings Technology*, *63*, 47–53.

Winchester, C., & Charles, M. (1992). *Waterborne nitrocellulose lacquer emulsion*. Eu Patent: 0,493,842 A2.

Worden, E. C. (1911). *Nitrocellulose industry: A compendium of the history, chemistry, manufacture, commercial application and analysis of nitrates, acetates and xanthates of cellulose as applied to the peaceful arts, with a chapter on gun cotton, smokeless powder and explosive cellulose nitrates*. Princeton: D. Van Nostrand Company., pp. 21–24.