Construction of h-BN Based Coating Towards The Flame Retardancy of Cotton Fabrics: Based on The Guidance of Mesoscopic Simulation

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Abstract. The employment of nanofillers for the enhancement of flame retardant of cotton fabrics was limited by the weak adherency, which is usually deal with additional adhesive coating. This paper investigates the adhesive of polydimethylsiloxane (PDMS) from the mesoscopic perspective, illustrates the adhesive mechanism of PDMS basing on the three key features: the binging energy, the radial distribution function, and hydrogen bond. Furthermore, based on the mesoscopic feasibility analyze, h-BN as well as the adhesive agent PDMS/PDA coating was fabricated to obtain the flame retardant cotton fabric. Comparing the Scanning electron microscopy and ATR-FTIR demonstrated that the flame retardant coating was successfully constructed on the substrate. The thermogravimetric analysis (TGA) and cone calorimeter (cone) confirmed the enhanced thermal stability and flame retardancy. The mesoscopic simulation and thermal analyze experiment (Scanning electron microscopy,ATR-FTIR,TGA) show PDMS employs a favorable adhesion agent for obtaining the better distribution state of h-BN than that of PDA-connected sample, which is responsible for improving flame retardancy.

1. Introduction

One hand, hexagonal boron nitride nanosheets (h-BN), a structural analogue of graphene, is superior to graphene, the predominant chemical inertness, ultra resistance to oxidation and environmentally friendly[1, 2]. The extreme electrical insulation of h-BN nanosheets has been developed and utilized in a wide range of technological applications [3]. Furthermore, for h-BN nanosheets, the layered structure and predominant thermal stability are potential to generate the flame retardant effect for polymer materials. On the other hand, Zotti.et.al found that the properties of PDMS, as an electrochromic material, employ a significant in electrochromic devices[4]. D Gregory.et.al considered the potential of PMDS, and he revealed that the anion determines the surface morphology of the film deposited on the electrode that illustrates the adsorption property [5]. Therefore, the adhesive effect of PDMS was anticipated for constituting the flame retardant coating.

Meanwhile, Alder and Wainwright first introduced the molecular dynamics method to study the interactions of hard spheres [6]. Yarovsky.et.al investigated the strength and molecular mechanisms of adhesion between two type substances using simulation [7]. With the rapid development of simulation technology, the mesoscopic simulation technology has become a mature path to illustrating the internal molecular mechanisms.

Therefore, this paper investigates the adhesive of PDMS basing on the mesoscopic simulation, illustrate the dynamic property of the PDMS adhesion. As a contrast, polydopamine as adhesive was used to cover onto the surface of cotton fabrics to conjugate h-BN. Furthermore, through the experimental method to fabricate the h-BN as well as the adhesive agent PDMS/PDA coating, and explore the employment of PDMS for the construction of h-BN based coating towards the flame retardancy of cotton fabrics.

2. Simulation

To illustrate the adhesive of PDMS and verify the PDMS coating feasibility, the mesoscopic simulations were carried in the Materials studio. For the Mesoscopic Dynamics (MD) simulation, we used the Nosé-Hoover-Langevin (NHL) method and the Berendsen method to control the temperature and pressure system. Moreover, to study the morphology and morphology of polymer material, the Dissipative Particle Dynamics (DPD) methods of computer simulation was utilized. Hoogerbrugge and Koelman [8] proposed the DPD method that is a mesoscopic simulation method for solving the thermodynamic behavior of complex fluids, which treats molecules as a mass or a bead and calculate the force per molecule group according to Newton's equation of motion. This paper builds the different ratio PDMS amorphous coating structures that including the 0，0.62，0.44 and 0.31-layer structure, which represents the different adhesive coating region. The simulation contains the optimal structure process and equilibrium simulation (NPT, NVT) repeatedly. Finally, the

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optimized structures were carried the DPD to acquire the mesoscopic parameters. The intermolecular interactions phenomena have appeared as follows in Figure 1.

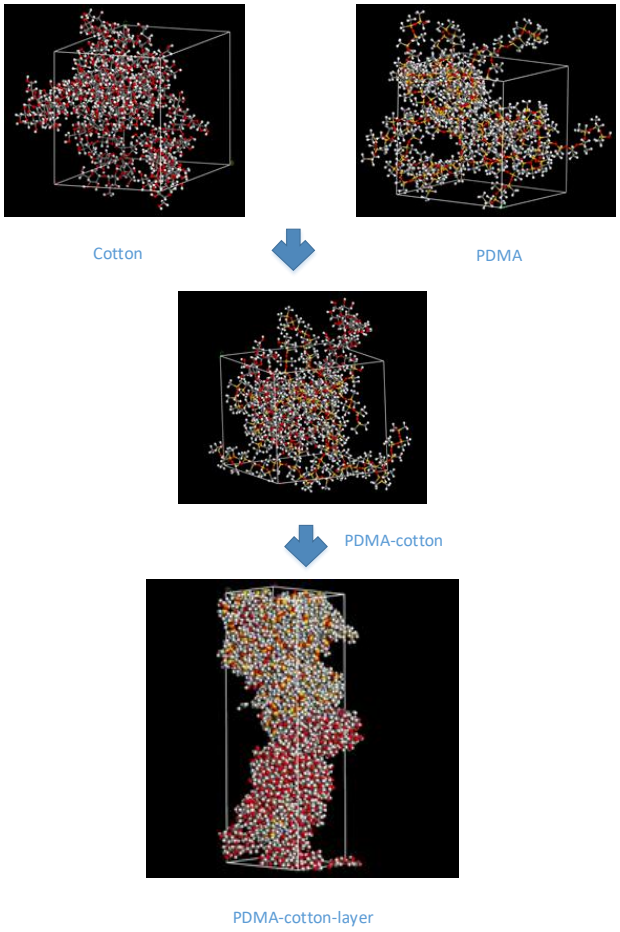

Figure 1. Molecular structure diagram.

In Figure 1, the molecule of the PDMS and cotton fabric appear the mutual attraction, and they connect eventually together in the room temperature.

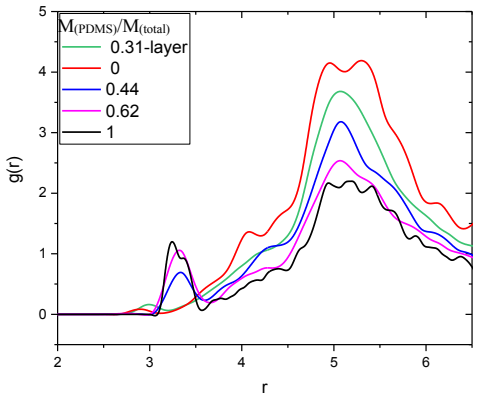

Figure 2. Radial distribution function.

In Figure 2, the radial distribution function g(r) can reveal the property of the interaction between non-bond atoms, and it is the characteristic physical quantity reflecting the microstructure of the material. It indicates that the probability density of another molecule distance r to a molecule. The compatible of the components is increasing with the decreasing of the value of the g(r), and vice versa. The radial distribution function shows increasing compatibility with the enhancement of PMDA, and the 0.31-layer construction also appears better results than the cotton for compatibility.

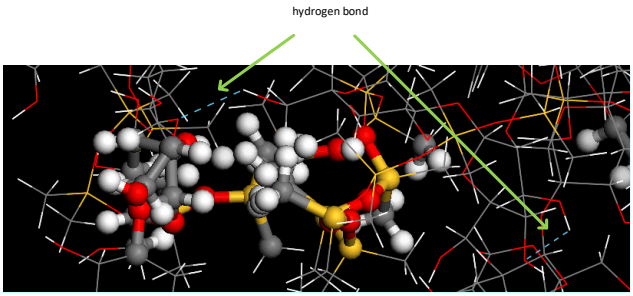

Figure 3. Hydrogen bond.

The hydrogen bond is a secondary bond that is weaker than a chemical bond and is similar to Van der Waals force according to the earlier studies. In Figure 3, the molecular structure appears some possible hydrogen bond which shows the molecules were strongly constrained to keep the concentrated state to form a small intermolecular distance that illustrates the effect of PDMS adhesive.

Table 1. Binging energy.

M(PDMS)/M(total)	binging energy(kJ/mol)	No-bond energy(kJ/mol)
0	79.32582833	302.7438
0.62	183.635018	668.0329
0.44	141.0566695	618.8785
0.31-layer	242.7200087	1163.826
1	178.0169483	917.0603

In Table 1, we can find that the binging energy and no-bond energy are increasing with the enhancement of PDMS content. Notable, the PDMS layer structure has maximum binging energy and no-bond energy. Moreover, the no-bond energy is higher than the binging energy that the PDMS enhances the intermolecular force for coating. It means that the PDMS with more surface active groups is more beneficial for the enhancement of interaction with other molecules. So far, we can confirm the PMDA can be used to constitute the coating. Therefore, we can carry the experiment to measure the flame retardancy of the PDMS/PDA for the PDMS/PDA coating.

3. Experiment

Cotton fabrics (100%, 220 g/m2) were supplied by the Shaoxing Manheng Textiles Company, China. Dopamine hydrochloride was offered by Sinopharm Chemical Reagent Co., Ltd., China. Poly (dimethylsiloxane) (PDMS) prepolymer (Sylgard184A) and the curing agent (Sylgard 184B) were supplied from Dow Corning Corporation (Shanghai,China). All the reagents were used as received. Hexagonal boron nitride (h-BN, AP) with a purity of 98.5% was purchased from Aladdin Industrial

Co., Ltd. (China), of which the average particle size was about 1 μm.

Firstly cotton fabrics was immersed in chloroform solution containing 2 wt% Sylgard 184A and 0.2 wt% Sylgard 184B for 2 min and subsequent dried at 80 oC for 2 h. Then, treated cotton fabrics were dipped into h-BN dispersion solution of 5 g/L (prepared by sonication for 2 h) for 2 min and then dried at 80 oC. The obtained samples in the first and second step were designed as Cotton-PDMS and Cotton-PDMS-hBN, respectively. The PDA-covered cotton fabrics was prepared in similar steps. Firstly cotton fabrics was immersed in DA solution, of which pH was adjusted to 8.5 by tris-HCl, for 2 h. Then, treated cotton fabrics were dipped into h-BN dispersion solution of 5 g/L (prepared by sonication for 2 h) for 2 min and then dried at 80 oC. The obtained samples in the first and second step were designed as Cotton-PDA and Cotton-PDA-hBN, respectively. The content of the coating on the fabric (weight gain) was calculated according to the following equation: Weight gain = (W1-W)/W × 100%, where W and W1 are the weight of the untreated and treated samples, respectively. The microstructures of the samples were characterized using an FEI Sirion200 scanning electron microscope (SEM). Measurements FTIR spectra were recorded on a Nicolet MAGNA-IR 750 FTIR spectrometer. The Thermogravimetric analysis (TGA) of the samples under nitrogen and air atmospheres were examined on a TGA-Q5000 apparatus (TA Instruments Inc., USA) from 50 to 700 ◦C at a heating rate of 20 ◦C/min. Combustion test was performed on a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660 standard procedures, with 100 × 100 × 0.5 mm3 specimens. Thermogravimetric analysis-infrared spectrometry (TG-IR) was carried out with a TGA Q5000IR thermogravimetric analyzer linked to a Nicolet 6700 FTIR spectrophotometer from 20 to 800 °C at 20 °C/min (N2 atmosphere, flow rate of 30 mL/min).

4. Results and discussions

In Figure 4 (a), SEM photograph of pure cotton fabric shows a smooth surface. However, similar appearance isn't observed in the SEM photographs of PDMS or PDA coated cotton fabrics and a much rougher surface is found (Figure 4 (b) and (d)). Meanwhile, the other samples containing h-BN presents circle-liked nanoparticles, which is attributed to h-BN itself (Figure 4 (c) and (e)). It's worth noting that h-BN nanosheets still present itself morphology in Cotton-PDA-h-BN. However, a similar phenomenon isn't found in Cotton-PDMS-h-BN, i.e. h-BN nanosheets were strongly absorbed onto the surface of Cotton-PDMS.

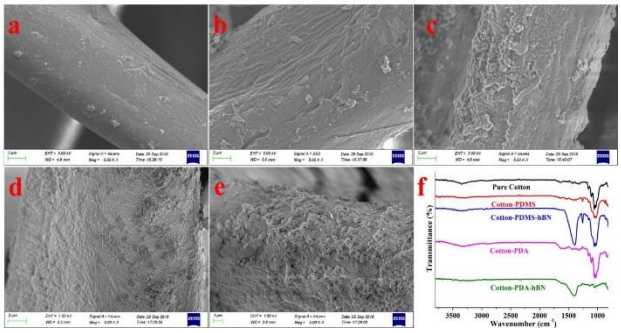

Figure 4. SEM images of Pure Cotton (a), Cotton-PDMS (b), Cotton-PDMS-hBN (c), Cotton-PDA (d), Cotton-PDA-hBN (e); (f) ATR-FTIR spectra of pure and coated cotton fabrics.

This result is consistent with the above simulation analysis which indicates that PDMS is a favorable adhesive. ATR-FTIR spectra can quantify the surface chemical structures of cotton fabrics which depends on measuring the changes in a reflected infrared beam from the materials. In Figure 4 (f), compared with pure cotton, PDA and PDMS-based coating have negligible change that shows the similar structure to cotton. Meanwhile, a new peak around 1260 cm-1 of Cotton-PDMS and Cotton-PDMS-h-BN that may be due to the stretching vibration of Si-O bond. More importantly, h-BN produces a new and strong peak in 1460 cm-1.

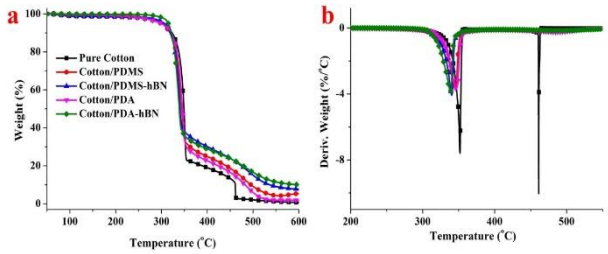

Figure 5. TG (a) and DTG (b) curves of the pure Cotton, Cotton/PDMS, Cotton /PDMS-hBN, Cotton /PDA, and Cotton /PDA-hBN.

TGA, a widely accepted tool for revealing the thermal behavior of the materials, can provide the curve of the weight loss with increasing temperature. As presented by Figure 5, the different materials are all beginning drastic pyrolysis when the temperature is over 300 oC. However, there is a difference between the cotton-PDMS-hBN and the pure Cotton. The weight loss is near to 5% before the sharp attenuation for pure Cotton, while Cotton/PDA-hBN almost keeps the initial weight that has high thermal stability. Moreover, it is obvious that PDMS-hBN and PDA-hBN can get high char residue. In Figure. 4 (b), we can find the peak and initial pyrolysis temperature for PDMS-hBN is lower than pure cotton's. It means that the PDMS-hBN and PDA-hBN reduce the combustible pyrolysis gas to avoid the violent combustion reaction.

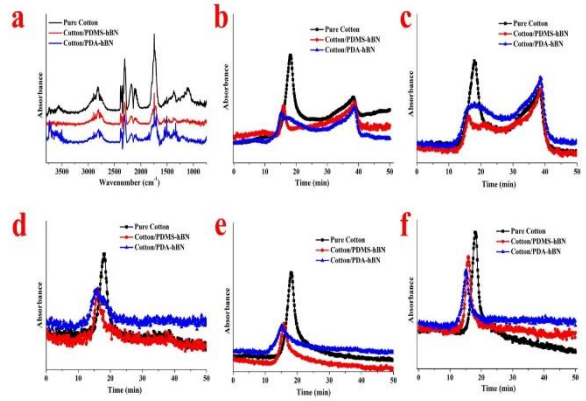

Figure 6. (a) FTIR spectra of the pyrolysis gaseous products emitted at the maximum degradation rate, (b) total absorbance of pyrolysis products, (c) CO, (d) CO_2, (e) carbonyl compounds, (f) hydrocarbon compounds of neat cotton fabrics, cotton-PDMS-hBN, and cotton-PDA-hBN.

In generally, TG-FTIR can analyze the gas products after thermal decomposition of materials, which is one path to study the thermal degradation process. Figure. 6 shows the absorbance of pyrolysis products for pure cotton fabric and PDMS-hBN/ PDA-hBN samples. The absorbance peaks of all samples are similar, indicating the surface modification didn't obviously change the decomposition reaction. The main production types include the CO, CO_2, carbonyl compounds, hydrocarbons. The strongest absorptions of all the pyrolysis appear when the time approach to 19 min. Comparing to the pure cotton, we can find the release peak is earlier in PDMS-hBN/PDA-hBN samples. It means that the coating weakens the external heat conduction toward to the cotton, and might absorb a part of the heat. Meanwhile, the peaks intensity of released gas products of Cotton-PDMS-hBN and Cotton-PDA-hBN samples is lower than pure cotton's. This phenomenon could demonstrate that the covered h-BN can hinder the thermal degradation process of cotton fabrics.

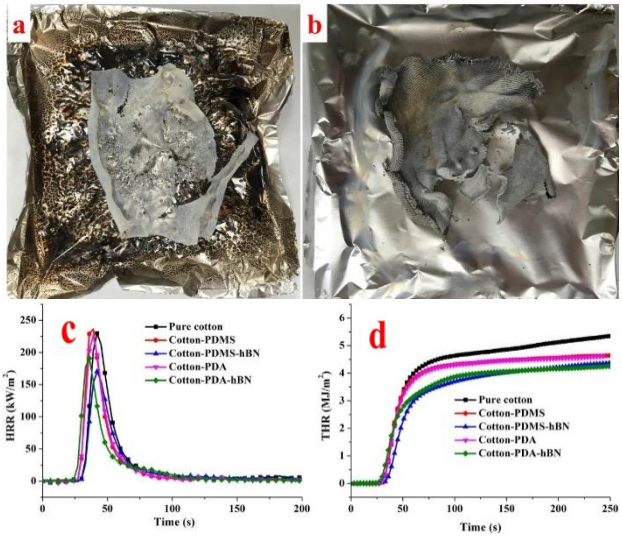

Figure 7. Char residue photographs of pure cotton fabric (a), Cotton-PDMS-hBN (b), (c) Heat release rate, (d) total heat release in cone test.

Cone calorimeter has been widely applied to measure release heat during the combustion process, which bases on the oxygen consumption principle. Figure 7. represents the heat release rate and total heat release of pure cotton and other samples. It is found that the only PDMS and PDA can not decrease the peak heat release rate (pHRR 230 kW/m2) of materials. This phenomenon is completely accepted due to the typical organic structure. Fortunately, PDMS/PDA has no acceleration for the combustion and the THR decrease from the 5.3 MJ/m2 to 4.6 MJ/m2. Notably, the introduction of h-BN restrains the heat release process of cotton fabrics, confirmed by decreased pHRR and THR. The lower PHRR and THR might be due to thermal insulation of h-BN, and PDMS-hBN appears better results (PHRR =170 kW/m2) that is the minimum in all samples and the other parameters are similar with the other samples) than other. It means the better adhesive effect PDMS make h-BN obtaining the uniform distribution onto the surface of cotton fabrics, thus causing the better flame retardancy.

5. Conclusion

Based on the mesoscopic simulation, PDMS can effectively exert the adhesive effect, improve the connection energy of the molecular and non-bond energy. It reduces the value of the radial distribution function, and enhance the interaction ability of cotton fabrics with other particles. ATR-FTIR results and SEM photographs confirm PDMS/PDA coating were successfully covered onto the surface of cotton fabrics. The connection effect of PDMS/PDA coating also employs which make h-BN covered onto the modified surface. As simulation analysis presents, the strong adhesion of PDMS obtained better distribution state of h-BN than that of PDA-connected sample. According to thermogravimetric analysis and cone results, PDMS/PDA as a coating adhesive agent has a weak effect to enhance the flame retardant and thermal stability of Cotton fabrics. However, after covered by h-BN nanosheets, the decreased heat release rate and mass loss rate was obtained in Cotton-PDMS-h-BN, rather than Cotton-PDA-h-BN. This result was due to the strong adhesive effect of the PDMS.

Acknowledgments

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