

Spectral Analysis of Poly (vinyl chloride) Film Enhanced by Modified Kaolinite

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Abstract- The aluminum-titanium compound coupling agent was used for surface organic modification of kaolinite and kaolinite/Poly (vinyl chloride) (PVC) composites were prepared by molten blending process. The performances of kaolinite and composites were investigated by fourier transform-infraredspectra (FTIR), thermogravimetric analysis (TGA), torque rheometer, environment scanning electron microscope (ESEM) and Ultraviolet visible (UV-vis) absorption spectra. With the FTIR and TGA results, it was confirmed that an organic coating layer was formed on the surface of kaolinite. Torque rheological plots show that the processability of modified kaolinite filled PVC was better than untreated kaolinite system. When filled with 10 wt% modified kaolinite, the comprehensive mechanical performance of PVC has achieved the best. ESEM images showed that modified kaolin can evenly disperse in PVC matrix. TGA and UV-vis spectrum analysis indicated that kaolin can improve thermal stability of PVC composite.

Keywords- Kaolinite; PVC; Processability; Thermal Stability; UV-Vis Spectra

I. INTRODUCTION

Polyester fabric coated PVC, with advantages of light weight, high strength, good air-tightness, easy welding and flame retardant, is widely used for various applications such as biogas engineering, inflatable boats, gym floors, tank liner, awning, truck cover and other covering materials for construction [1-4]. In these areas, PVC films of the surface layer are vulnerable to various kinds of attacks over long periods of outdoor exposure, such as the degradation of light, heat and oxygen, the erosion of acid or alkali and the wear of external stress, all of which could damage surface integrity of PVC films. When the PVC films happened to broke, the polyester fabric had been exposed to environment, then the mechanical performance of composites degraded and the use life would reduce. Therefore, the research and development of PVC films with excellent performance are becoming more and more important.

PVC is controllable to classify as soft, semi-hard and hard material by varying the amount of plasticizer [5]. The behaviour of PVC in thermal decomposition can be divided into two stages: stepwise and catalytic pyrolysis [6]. The dehydrochlorination of PVC long chain takes place at a lower temperature (300°C), and HCl has a catalysis on the thermal degradation of PVC resin [7].

Kaolinite, an important clay mineral, has a wide application in industry, such as pigment and filler for paper, rubber and plastic, intercalated kaolinite/polymer composites and the precursors of inorganic nanomaterials with specific structure [8-10]. In polymeric matrixes, the applications of kaolinite show numerous advantages, such as white shade, flame resistance, toughness, chemical inertness, lower shrinkage, lower plate out, low abrasion and low conductivity of thermal and electrical. When calcinated at 600°C, kaolinite releases crystal water and results in a product of metakaolinite with amorphous and porous structure. Calcination treatment of kaolinite can improve the acid reactivity of aluminum oxide [11], which gives good results as HCl scavenger in PVC matrix.

In this work presented here, the aluminum-titanium compound coupling agent was used for surface organic modification of kaolinite and kaolinite/PVC composites were prepared by molten blending process. It was expected that the modified kaolinite could be dispersed well in PVC. The effects of kaolinite on processability and mechanical properties of PVC were investigated. With UV-vis spectra analysis, it was investigated on thermal aging action of kaolinite/PVC composites in different conditions.

II. EXPERIMENTAL

A. Materials

Calcined kaolinite (DB-2500) was supplied by LongYan Kaolin-clay Co., Ltd. PVC resin (SG-3) was supplied by Shenyang Chemical Industry Co., Ltd. The coupling agent of aluminum-titanium compound (1618) was purchased from Nanjing JingTianWei Chemical Industry Co., Ltd. Diisononyl phthalate (DINP) was kindly donated by ZhenJiang LianCheng Chemical Industry Co., Ltd. Thermal stabilizers used were Liquid and Powder barium zinc stabilizer, the former was supplied by ChaoHu XiangFeng plastic additives Co., LTD, and the latter was supplied by ChangZhou JiaRenHe Chemical Co., LTD.

B. Organic Treatment of Calcined Kaolinite

The reaction was performed in a temperature-controllable high speed mixer. Kaolinite was dried for 12 h at 80°C before the organic modification reaction. Then, 400 g of kaolinite and 6 g compound coupling agent were poured into mixer. The mixture was stirred for 15 min at 110°C.

C. Preparation of Kaolinite/PVC Composites

The kaolinite content in the composites was 0, 5, 10, 15, 20 wt%. 2 parts of liquid barium zinc stabilizer, 1 part of powder barium zinc stabilizer and 45 parts of DINP were added to 100 parts of PVC by using a torque rheometer. Before processing, the mixture of PVC and additives should be homogeneous mixing in a chinese medicine crusher. After the blends reached plasticizing balance in the torque rheometer, the samples of PVC composites were pressed into film with a certain thickness, 0.3 mm for mechanical properties tests and 80 µm for UV-vis spectra analysis, on the double roller.

D. Characterization

The FTIR were recorded for modified kaolinite with a Perkin-Elmer Lambda 900 FTIR spectrometer with KBr pellets. The range of scanning is 4000~400 cm⁻¹.

The TGA could be conducted on Netzsch STA449C thermal system in N₂ atmosphere scanning from room temperature to 800°C at a heating rate of 10°C/min.

The mechanical properties of composites were tested by a CMT6104 electronic universal testing machine. Tensile strength tests were conducted according to GB/T 1040.3-2006 and tear strength tests followed GB/T 16578.1-2008.

The morphology of samples was characterized by a Philips-FEI XL30 ESEM at an accelerating voltage of 20 kV.

With air as a reference, optical spectra of PVC films were recoded with a UV-2450 UV-vis spectrophotometer.

III. RESULTS AND DISCUSSION

A. Organic Treatment of Calcined Kaolinite

Fig. 1 presents the FTIR spectrum for calcined kaolinite, modified kaolinite and aluminium titanium compound coupling agent. The spectra of calcined kaolinite (Fig. 1a) shows relatively simple pattern in the region of low wavenumbers, which reveals that the peaks at 1074 and 472 cm⁻¹ correspond to the distortion of the structure of original sheets. The peak at 799 cm⁻¹ ascribes to free silica or quartz impurities in kaolinite. 539 cm⁻¹ attributes to Si-O-Al bond [12]. The relatively broader OH stretching bands with weak absorption peaks at 3697 and 3622 cm⁻¹ was observed obviously, which attributed to the structural water release of kaolinite after calcination. The spectra of aluminum-titanium coupling agent (Fig. 1c) showed the characteristic of -CH₃ and -CH₂ stretching vibrations at 2918 and 2850 cm⁻¹. In the case of modified kaolinite (Fig. 1b), the appearance of -CH₃ and -CH₂ at 2920 and 2853 cm⁻¹ indicates the organic treatment was successful on the surface of kaolinite.

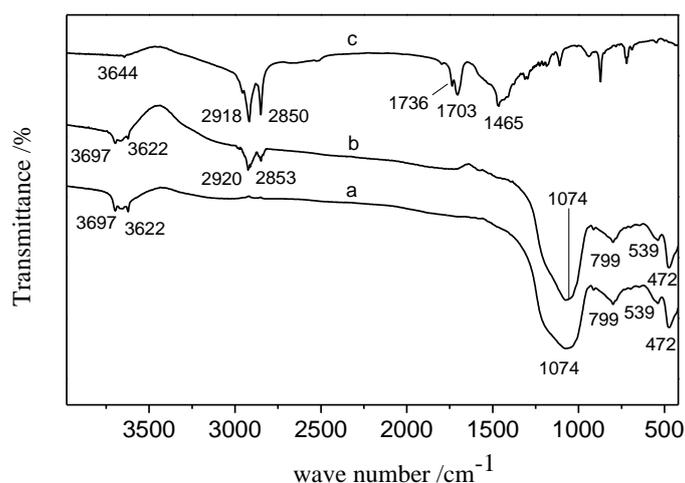


Fig. 1 FTIR patterns of (a) calcined kaolinite, (b) modified kaolinite and (c) aluminum-titanium coupling agent

Fig. 2 shows the TGA results for calcined kaolinite, modified kaolinite and aluminum-titanium compound coupling agent. In calcined kaolinite sample, the weight loss was divided two stages (Fig. 2a). The first one was between room temperature and

200°C with a slow loss, which was assigned to the elimination of physisorption water molecules on surface of the metakaolinite. Another one started at 500°C with obvious loss last to 800°C, which attributes to the removal of hydroxyl groups or structure water molecules bonded to the layers. As shown on Fig. 2b, the modified kaolinite exhibits relative rapid weight loss feature between 287.7~342°C attributed to the thermal decomposition of coupling agent. In the case of coupling agent shown in Fig. 2c, the first decomposition step starts at 180°C and lasts to 480°C. Another weight loss was present at 600~720°C. The initial decomposition temperature of coupling agent has increased about 108°C, which corresponded to the enhanced binding force between coupling agent and kaolinite surface by composite effect.

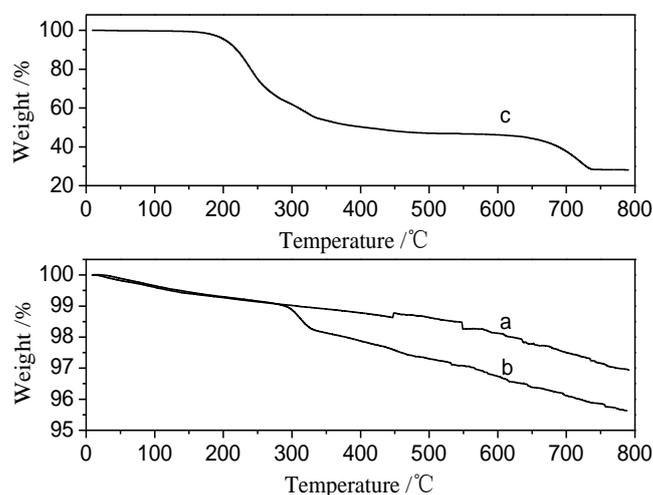


Fig. 2 TGA curves for (a) calcined kaolinite, (b) modified kaolinite and (c) aluminum-titanium coupling agent

Observations of the morphology of the calcined kaolinite and modified kaolinite were clearly seen in ESEM images (Fig. 3). Before modification, the aggregation of kaolinite with more than 10 μm was easily observed in Fig. 3a. Through coupling agent modification process, kaolinite pieces of layers became smaller and particle size distribution is more uniform (Fig. 3b). It can be attributed to two aspects: the kaolinite aggregation was broken up by the shear forces of mixing and kaolinite coated with coupling agent can reduce the reuniting chance of kaolinite particle after further spread by mechanical force.

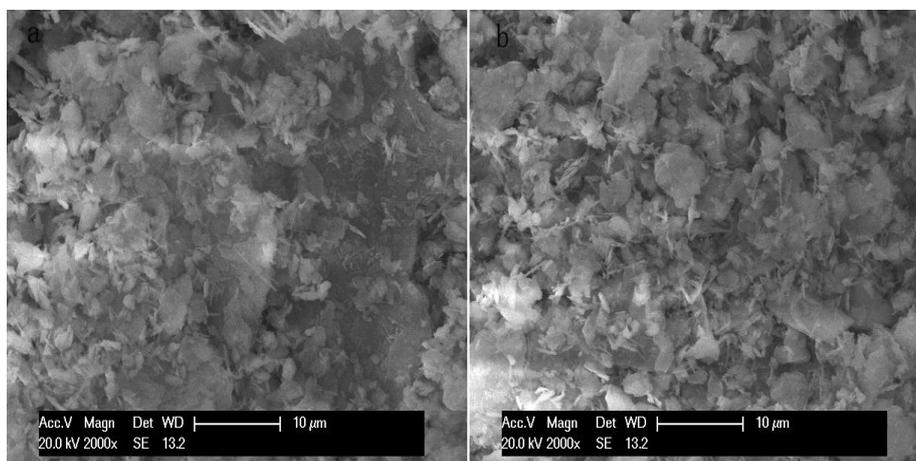


Fig. 3 ESEM images of (a) calcined kaolinite and (b) modified kaolinite

B. Torque Theological Properties of Composites

Fig. 4 shows the torque-time plots of PVC composites, at 100 rpm. With an increase of kaolinite content, there was an increase tendency of the maximum torque and balance torque of the blends. When the kaolinite is introduced in the PVC matrix, the solid particles offer an additional resistance to the rotator and therefore the torque increases. Also, it has been shown that PVC filled with modified kaolinite has lower of maximum torque and balance torque compared to untreated kaolinite. As is shown in Table 1, the balance torque of PVC filled with 10 wt% modified kaolinite which is equal to the PVC without kaolinite. It can be attributed to good compatibility with PVC when the blends completely melt and reach again a stabilized morphology [13-14]. To a certain extent, the modification of fillers can reduce the negative influence of processing performance.

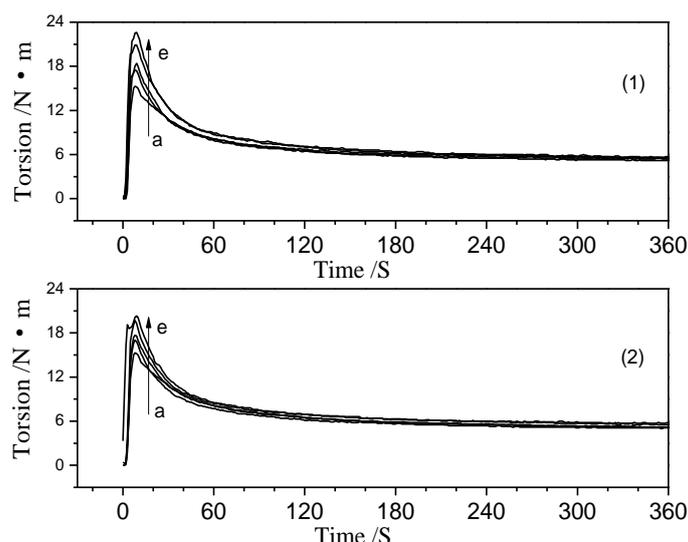


Fig. 4 Torque rheological curve of PVC filled with different wt% (a-0, b-5, c-10, d-15, e-20) of (1) untreated kaolinite and (2) modified kaolinite

TABLE 1 TORQUE RHEOLOGICAL PROPERTIES OF KAOLINITE/PVC COMPOSITES

Composites	Maximum torque (N m)	Balance torque (N m)	Balance temperature (°C)
m(K)/m(PVC) (0%)	15.3	5.2	175.5
m(MK)/m(PVC) (5%)	17.0	5.1	175.4
m(MK)/m(PVC) (10%)	17.7	5.2	176.2
m(MK)/m(PVC) (15%)	19.7	5.7	175.8
m(MK)/m(PVC) (20%)	20.3	5.5	176.6
m(UK)/m(PVC) (5%)	17.5	5.4	175.7
m(UK)/m(PVC) (10%)	18.4	5.5	175.9
m(UK)/m(PVC) (15%)	20.9	5.5	176.9
m(UK)/m(PVC) (20%)	22.6	5.7	177.0

K: kaolinite; MK: modified kaolinite; UK: untreated kaolinite

C. Mechanical Properties of Composites

From Table 2, with an increase of kaolinite content, the mechanical properties of composite appear increased at first and then decreased. When kaolinite content was 10 wt%, tensile strength and break elongation of composite reached to the maximum namely 16.5 MPa and 343.2%. Tear strength of PVC filled with 5 wt% kaolinite reached to the maximum of 47.7 kN/m. Therefore, filled with 10 wt% modified kaolinite, the comprehensive mechanical performance of PVC has achieved the best. Namely tensile strength of the composite increased from 15.8 MPa of pure PVC to 16.5 MPa, break elongation from 263.7% to 343.2%, and tear strength from 37.0 kN/m to 46.8 kN/m. When kaolinite content was more than 10 wt%, the mechanical properties of composite began to fall down. With the content of 20 wt%, the tensile strength, break elongation and tear strength of PVC composite decreased slightly 0.8 MPa, 11.1% and 2.7 kN/m compared with that of pure PVC. It has been showed that low addition of modified kaolinite gave better strength and toughness. It can attribute to a good dispersion of modified kaolinite platelets in PVC matrix. With an increase of the kaolinite content, the particle is hard to further spread. As the aggregation of kaolinite became more serious, there was a negative effect of the mechanical properties of composite.

TABLE 2 MECHANICAL PROPERTIES OF MODIFIED KAOLINITE/PVC COMPOSITES

Composites m(MK)/m(PVC)	Tensile strength (MPa)	Break elongation (%)	Tear strength (kN/m)
0%	15.8	263.7	37.0
5%	16.2	311.4	47.7
10%	16.5	343.2	46.8
15%	15.4	269.7	40.3
20%	15.0	252.6	34.3

MK: modified kaolinite

Fig. 5 represented the morphologies of fractured surfaces of kaolinite/PVC and modified kaolinite/PVC composites. Kaolinite without organic modification could form some aggregation with 1~5 μm in PVC matrix (Fig. 5a). Through modification processing with aluminium-titanium compound coupling, kaolinite can be more evenly dispersed in PVC matrix

and reunion phenomenon has greatly abated. Most kaolinite platelets appeared as exfoliated slice layer structure were observed clearly in the image of Fig. 5(b). These confirmed that the modified of kaolinite using coupling agent was effective to improve the dispersion of kaolin in PVC matrix.

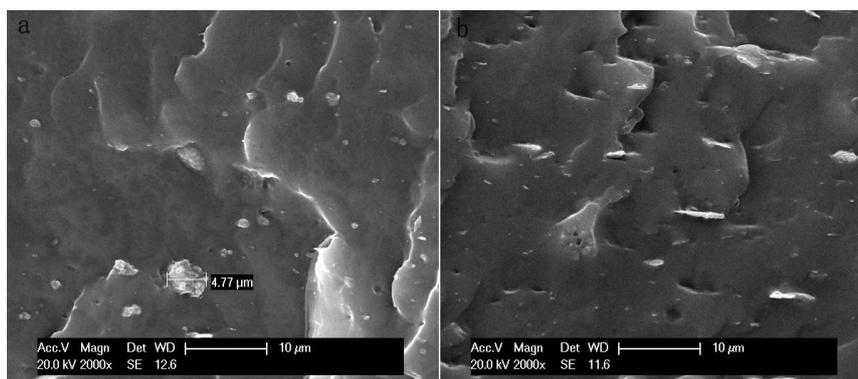


Fig. 5 ESEM images of fractured surfaces of PVC films filled with 10 wt% (a) untreated and (b) modified kaolinite

D. Thermal Properties of Composites

The thermogravimetric analyses curves of pure PVC film and kaolinite/PVC composite are given in Fig. 6. In the case of pure PVC, the weight loss was clearly observed at two stages (Fig. 6a). The first one was between 150°C and 350°C corresponding to the dehydrochlorination of PVC long chain and the weight loss by the degradation of organic processing agents [6]. Another one started at 428°C with obvious loss last to 535°C, which attribute to the formation of alkyl aromatics with a residual char. Kaolinite/PVC composite has a similar thermal weight loss curve to pure PVC, but the PVC composites have an obvious degradation start at 235°C while pure PVC is 224°C. It corresponded to the improving of thermal stability of PVC filled with kaolinite. Aluminum oxide with acid reactivity of calcined kaolinite can absorb the HCl gas that released from the thermal degradation of PVC, which inhibit the catalysis on dehydrochlorination to a polyene structure. At the second stage, the carbon residue of pure PVC film is about 11%, while the carbon residue of PVC filled with 10% modified kaolinite is about 20%. Considering to the weight loss of modified kaolin between room temperature to 800°C is about 4.4% (Fig. 2), the carbon residue has increased about 0.88% of PVC composite calculated in theory. To a certain extent, kaolinite can improve the thermal stability of PVC composites.

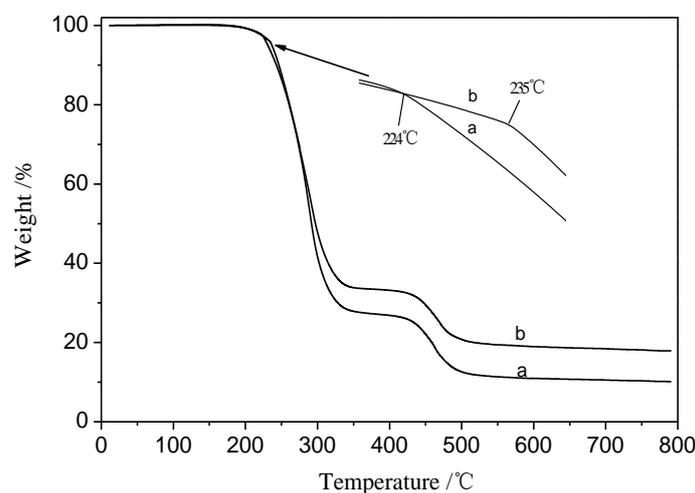


Fig. 6 TGA curves for (a) pure PVC and (b) PVC filled with 10 wt% modified kaolinite

Fig. 7 shows UV-vis spectrums of pure PVC film and modified kaolinite/PVC composite for different thermal aging time. In previous reports [15, 16], there is a corresponding relation between UV-vis absorption wavelength and chain length of conjugated diene. The n of $\text{H}-(\text{CH}=\text{CH})_n-\text{H}$ ranging from 3~10, the absorption wavelength is respective corresponding to 268, 304, 334, 364, 390, 410, 428, 447 nm. From Fig. 7(1a) and 7(2a), it was observed that both of them have an obvious absorb peak around 348 nm, it may be attributed to the present of DINP in PVC formulas. With increasing of thermal aging time, the concentrations of the conjugate structure with 4-7 carbon atoms are significantly increased in pure PVC. Correspondingly, in Fig. 7(1b~d), the absorption strength enhances unceasingly in the wavelength region of 300 nm to 400 nm. From Fig.7(2b~d), there was a similar growth trend of the conjugate structure in system of PVC filled with 10 wt% kaolinite, but the absorbing

intensity in kaolin/PVC composite is inferior to pure PVC. It has been shown that kaolinite has a function of inhibiting the catalysis on degradation process. The synergy effect of kaolinite in PVC system with barium zinc stabilizer can further improve thermal stability of the system.

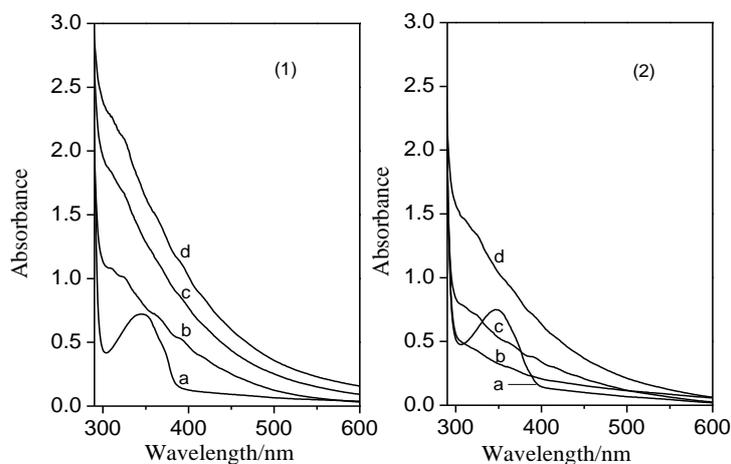


Fig.7 UV-vis spectrums of (1) pure PVC and (2) PVC filled with 10 wt% modified kaolinite for different aging time:a-0,b-30,c-60,d-90 min

Fig.8 shows UV-vis spectrums of modified kaolinite/PVC composite with different kaolinite content for aging 90 min. The thermal stability of the PVC system has been improved by filling with kaolinite. When PVC filled with 15 wt%, the absorbing intensity reached to the lowest. This means that the content of the conjugated double bonds was lowest. Along with an increase of the content of kaolinite (from 0 to 15 wt %) in PVC, the thermal stability became better and better. When the kaolinite content was 20 wt%, the enhancement effect of thermal stability was slightly less than the system of 15 wt%. Filled with much more kaolinite, it will affect its dispersion properties in PVC system. The surface area decreased as the reunion of kaolinite became more serious, which can reduce the absorption efficiency of HCl.

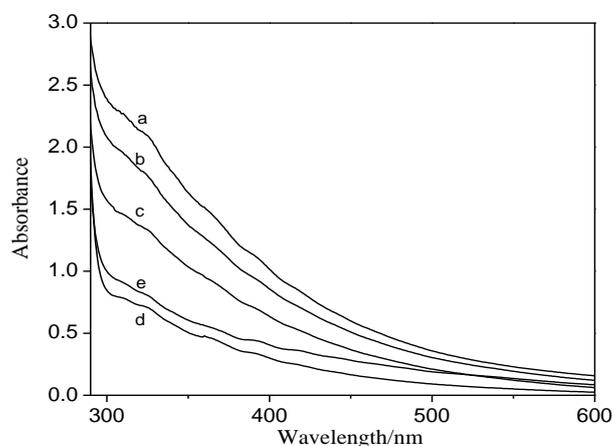


Fig. 8 UV-vis spectrums of PVC filled with different wt% (a-0,b-5,c-10,d-15,e-20) modified kaolinite for aging 90 min

IV. CONCLUSIONS

Organic treatment of kaolinite with aluminium-titanium coupling agent can restrain the reunion of kaolinite particles. Scanning electron microscopy image showed that modification can improve the dispersion of sheet kaolinite in PVC. When kaolinite content was 10 wt%, the comprehensive mechanical properties of composite materials could achieve to the optimal state. Tensile strength, break elongation and tear strength were increased respectively by 0.7 MPa, 79.5% and 9.8 kN/m. The PVC system filled with calcined kaolinite showed better thermal stability. It can absorb hydrogen chloride gases, which emerged by dehydro-chlorination of the long chain in thermal degradation process of PVC.

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