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Calculation of the Reactivity of Alkyl Ketene Dimer with Ethanol and the Characterization of Reaction Products

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The structure of alkyl ketene dimer was built by Gauss view. Gaussian03 quantum chemistry packages were used for quantitative calculation of alkyl ketene dimer and alcohol. The DFT was chosen to optimize the ground state geometries by B3LYP basis set in the 6-311G(d,p) level. The Mulliken charge distribution, energy and frontier molecular orbital characteristics were calculated. It was shown that C(54) of lactone ring had a higher positive charge which was 0.411128 C. The frontier molecular orbital indicated that the activity of alkyl ketene dimer was mainly focused on the lactone ring. Ethanol was chosen to react with alkyl ketene dimer.The reaction products were characterized by FTIR, NMR and SEM.

Key Words: Alkyl ketene dimer, Gauss view, Gaussian 03, Frontier orbital theory.

INTRODUCTION

Alkyl ketone dimer (AKD) is an ideal neutral paper making sizing agent, which is widely used in the paper industry to increase the paper hydrophobicity and improve its printability[1-3]. Super water-repellent surfaces showing a contact angle of 150º for water droplets can be made of alkyl ketene dimer[4-8]. Alkyl ketene dimer contains two kinds of groups: one is long-chain alkyl that contains 12 to 20 carbon atoms which can give the alkyl ketene dimer good hydrophobicity and another is the lactone ring.

All of the alkyl ketene dimer can not be extracted with organic solvents from the paper sized with alkyl ketene dimer. We speculated that part of the alkyl ketene dimer can not be extracted must have had irreversible chemical reaction with fibre.As a reactive functional group, the lactone ring can react with hydroxyl groups of fibre to produce irreversible β-keto esters that can be fixed on the fibre. This mechanism was called esterification reaction mechanism[9,10]. The assumed reaction mechanism was accepted by many experts. However, there is no reliable convenient means used for proving the existence of β-keto ester in the paper sized by alkyl ketene dimer. Peter[11] considered that esterification reaction mechanism can not explain why only a small amount of alkyl ketene dimer modified fibers (AMF) can make all the fibers to produce uniform water resistance and it also can not explain the migration phenomenon of alkyl ketene dimer. Isogai[12] considered that alkyl ketene dimer was only adsorbed on the surface of fiber and filler. Therefore, there is controversy about the alkyl ketene dimer sizing mechanism. At present, the main differences include following aspects. (1) whether alkyl ketene dimer and cellulose fibers can react, (2) the reaction conditions, (3) the extent of reaction, (4) the effect of extent of reaction on the sizing performance.

Gaussian is a powerful package of quantum chemistry. Molecular input to the software is transformed into Schrodinger equation. And the results by solving the equation can help us to understand the molecular properties such as the energy structure and molecular orbital, *etc.*[13,14]. Recently, density functional theory has been widely applied to study electronic structure of solids and molecular state. Compared with *ab initio* and semi-empirical methods, DFT was widely used due to high computational accuracy and fast computation speed. DFT can be used for the calculation of larger molecules because that the computation increase with the three cubed of the number of electrons.

Gaussian03 quantum chemistry package is used to optimize and calculate the structure of alkyl ketene dimer. The reactivity of alkyl ketene dimer was analyzed by calculated frontier orbital theory and charge density. But alkyl ketene dimer is difficult to react with fiber. In addition, the reaction products are difficult to separate from reactants. It is the hydroxy group that react with alkyl ketene dimer. Therefore, we chose some substances containing hydroxyl group that can react with alkyl

ketene dimer to simulate the reaction. In the research, we select the ethanol as solvent. Because ethanol have a hydroxy, but even more important, the reaction products are easy to separate from reactants. Then, the reaction products are characterized by FT-IR, ^{13}C NMR, SEM. In subsequent studies, we will choose starch, guar gum, *etc.* to react with alkyl ketene dimer. By analyzing the reactivity of high polymer and alkyl ketene dimer, We further simulate the process of sizing. Finally, fiber is used to react with alkyl ketene dimer. This methods here has not been published so far.

EXPERIMENTAL

A commercial alkyl ketene dimer wax was supplied by Suzhou Tianma fine chemicals Co., Ltd.(Jiangsu,China) and used without further purification. Ethanolwas commercially available and used without further purification. Cationic starch solution (25 %) was supplied by Aodong chemicals Co., Ltd. (Tianjin, China).

Infrared spectra were recorded using a FTIR spectrometer (TENSOR27, Bruker, German) in the range of 4000-500 cm^{-1}. The NMR spectra were recorded on a BRUKER AC-500 (Bruker, German) spectrometer. Images of the surfaces of sized paper were taken using a field-emission scanning electron microscope (JSM-6700F, JEOL, Janpan) after coating the samples with a thin layer of sputtered alloy of gold and palladium.

Structure of alkyl ketene dimer: The structure of alkyl ketene dimer is mainly composed of two cetyl and a lactone ring, as shown in Fig. 1.

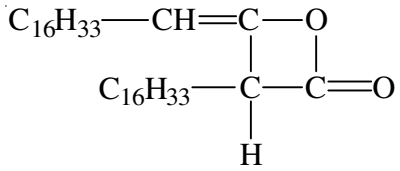

Fig. 1. Structural formula of alkyl ketene dimer

The structure of alkyl ketene dimer was built in Gauss View and then quickly optimized the molecular geometry. The atoms were marked using arabic numerals, as shown in Fig. 2.

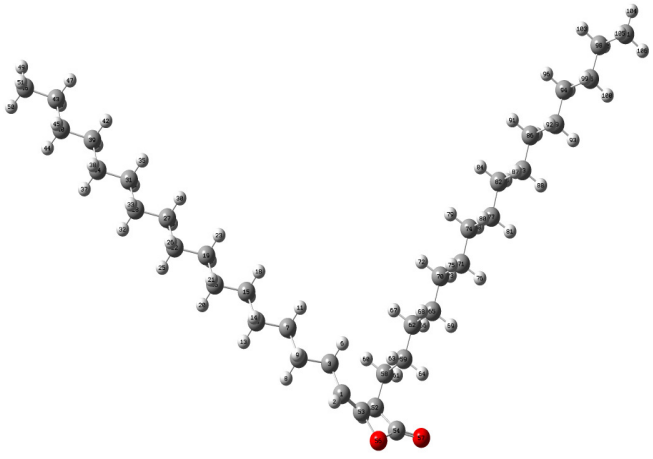

Fig. 2. Three-dimensional structure of alkyl ketene dimeralkyl ketene dimer

Gauss calculation of alkyl ketene dimer: Gauss view can directly generate input files for Gaussian calculations. Computer installed gauss view and Gaussian03 can calculate directly after quick optimization. The energy of alkyl ketene dimer molecules was calculated by density functional theory (DFT), B3LYP basis set in the 6-311G(d,p) level. The molecular geometry, atomic charge density and frontier molecular orbital were obtained. Calculation involved in 106 atoms, 1092 basis functions, 1760 primitive gaussians, of which contained 150 occupied orbit, 150 α-electrons, 150 β-electrons. The total charge and multiplicity of the system was respectively 0 and 1.

Reaction of alkyl ketene dimer with ethanol: Alkyl ketene dimer was melt in a beaker at 60 ºC. The melted alkyl ketene dimer (5 g) was put into a four mouth flask equipped with a reflux condenser and a thermometer. Ethanol (30 g) was poured into the four mouth flask. The mixture was reacted, with stirring, at 80 ºC for 12 h. The mixture was then washed and dried in an electric oven at 60 ºC for 3 h.

Emulsion of alkyl ketene dimer modified by ethanol: Modified-alkyl ketene dimer (20 g) was melted at 60 ºC. Water (160 g) and cationic starch solution (20 g) was pre-heated at 60 ºC. Cationic starch solution was slowly added to modified-alkyl ketene dimer in a plastic beaker. The mixture was sheared with a shearing velocity of 4000 rpm. Then part of the water (about 30 g) was slowly add to the mixture, the w/o emulsion could be prepared. The remaining water was added after 1 min. Then high-speed sheared (10000 rpm) for 10 min, product was quickly cooled. The o/w emulsion was finally changed into o/w emulsion.

Process of sizing: Surface sizing starch solution was prepared according to a reported method as follows. Surface sizing starch (40 g) and deionized water (460 g) were put into a neck flask equipped with a reflux condenser and a thermometer. The mixture was stirred at 95 ºC for 0.5 h. The ratio of surface sizing starch to modified-alkyl ketene dimer emulsion was 50:3. The mixture was stirred in a beaker for 10 min at 60 ºC.

Sizing agent was coated on the body paper using the 2 # coating rod on automatic coating machine, coating weight was *ca.* 6 g/m^2. The paper was dried in drying oven for 10 min. Cobb value was measured by surface absorption according to a reported method as follows. Paper was cut to a wafer whose diameter was125 mm. Weighing the dry weight of the wafer (w_1). Then, the wafer was placed in the Cobb absorption detector to absorb water for 1 min. Water of the surface was absorbed by filter paper. Weighing the wet weight of the wafer (w_2). Cobb value was calculated by the following formulae:

$$Cobb = (w_2 - w_1) \times 100\ \% \qquad (1)$$

RESULTS AND DISCUSSION

Gaussian calculation of Mulliken charge distribution: Mulliken charge distribution of alkyl ketene dimer was calculated by Gaussian03 (Table-1). Compared to other atoms, (54) C atoms has the largest positive charge, which is the point of necleophilic reaction. In the reaction process that is controlled by charge, if the atom has more negative charges than the other atoms, it is more likely to be attacked by electrophilic reagents.

TABLE-1
MULLIKEN CHARGE DISTRIBUTION OF ALKYL KETENE DIMER

No.	Atom	Charge	No.	Atom	Charge	No.	Atom	Charge	No.	Atom	Charge
1	C	-0.162194	28	C	-0.213775	55	H	0.147976	82	C	-0.206804
2	H	0.111738	29	H	0.103130	56	O	-0.346773	83	C	-0.206101
3	C	-0.169205	30	H	0.102921	57	O	-0.311740	84	H	0.103522
4	C	-0.240184	31	C	-0.199438	58	C	-0.175050	85	H	0.102874
5	H	0.127816	32	H	0.103961	59	C	-0.201552	86	C	-0.206013
6	H	0.128706	33	H	0.103268	60	H	0.120239	87	H	0.103535
7	C	-0.199359	34	C	-0.212709	61	H	0.124702	88	H	0.103315
8	H	0.114422	35	H	0.102987	62	C	-0.221806	89	C	-0.206788
9	H	0.107382	36	H	0.103525	63	H	0.127363	90	H	0.103102
10	C	-0.216491	37	H	0.104004	64	H	0.105408	91	H	0.103383
11	H	0.106190	38	H	0.103528	65	C	-0.198562	92	H	0.103683
12	H	0.107121	39	C	-0.200671	66	H	0.104565	93	H	0.103444
13	H	0.104469	40	C	-0.211562	67	H	0.110242	94	C	-0.204225
14	H	0.104573	41	H	0.103774	68	H	0.109952	95	C	-0.208586
15	C	-0.198016	42	H	0.102952	69	H	0.104815	96	H	0.103221
16	C	-0.214567	43	C	-0.228345	70	C	-0.214186	97	H	0.103211
17	H	0.104096	44	H	0.103615	71	C	-0.201927	98	C	-0.229699
18	H	0.104417	45	H	0.103091	72	H	0.105742	99	H	0.103248
19	C	-0.198090	46	C	-0.286215	73	H	0.103672	100	H	0.103151
20	H	0.103810	47	H	0.105483	74	C	-0.209165	101	C	-0.285432
21	H	0.103881	48	H	0.105901	75	H	0.105310	102	H	0.105592
22	C	-0.214139	49	H	0.103107	76	H	0.103482	103	H	0.105532
23	H	0.103187	50	H	0.100533	77	C	-0.204803	104	H	0.102828
24	H	0.103212	51	H	0.100199	78	H	0.103118	105	H	0.100437
25	H	0.103706	52	C	0.229318	79	H	0.104106	106	H	0.100235
26	H	0.103574	53	C	-0.278515	80	H	0.104018	–	–	–
27	C	-0.198420	54	C	0.411128	81	H	0.103361	–	–	–

On the contrary, it is more likely to be attacked by nucleophiles. The oxygen atoms (56) O and (57) O have the larger negative charge that may be the active site of the electrophilic reaction. Therefore, it can be speculated that the (54) C of alkyl ketene dimer may react with nucleophilic reagent. This active sites are located in the lactone ring of alkyl ketene dimer, In other words, compared to other atoms, lactone ring has a higher reactivity. As a nucleophile, ethanol has the tendency to react with alkyl ketene dimer.

Gaussian calculation of frontier orbital: In the system of alkyl ketene dimer, there are 1092 orbitals that contain 150 occupied molecular orbitals. No. 150 is the highest occupied molecular orbital, No. 151 is the lowest unoccupied molecular orbital. The calculated orbital energy near the frontier orbitals are shown in Table-2. E_{HOMO} =-0.24611au, E_{LUMO} = -0.03749au, E_{LUMO}-E_{HOMO} = 0.20862au. Stability of chemical compound is closely related to HOMO-LUMO gap of frontier orbital and the absolute value of HOMO orbital energy. Generally speaking, the greater absolute value of HOMO orbital energy means that the ground state stability of the compound is higher and the greater HOMO-LUMO gap is, the stronger stability of molecular is. It means that ground state structure of alkyl ketene dimer is apt to react with nucleopilic reagent. Beause of E_{LUMO} < 0, in the reaction process, alkyl ketene dimer could easily obtain electron.

Molecular orbital theory suggests that the HOMO, LUMO and the molecular orbital around the HOMO, LUMO have the greatest influence on the molecular activity. Therefore, the nature of frontier orbitals can provide important information. The electron energy of HOMO is the highest, so it is the most active electron. However, The electron energy of LUMO is the lowest in all unoccupied orbitals and it is likely to accept electrons. Consequently, these two orbitals determine the ability of gaining, losing and transfering electrons. These two orbitals also determine the spatial orientation and other important chemical properties. Figs. 3 and 4 are the highest occupied orbital and the lowest unoccupied molecular orbital respectively. As can be seen, HOMO and LUMO are mainly contributed by the lactone ring, which means that the lactone ring is the reactivity bit of alkyl ketene dimer.

TABLE-2
FRONTIER ORBITAL ENERGY OF
ALKYL KETENE DIMER (au)

	NHOMO	HOMO	LUMO	NLUMO
Orbital	149	150	151	152
Energy	-0.26634	-0.24611	-0.03749	0.00292

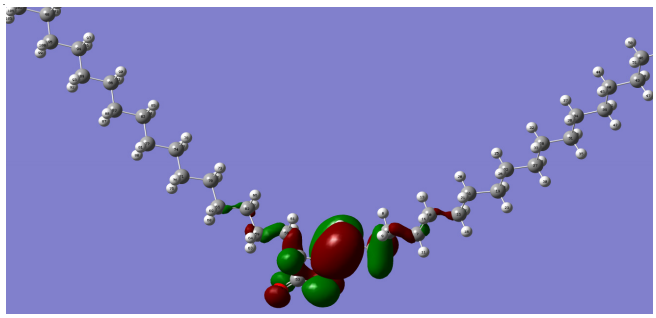

Fig. 3. HOMO

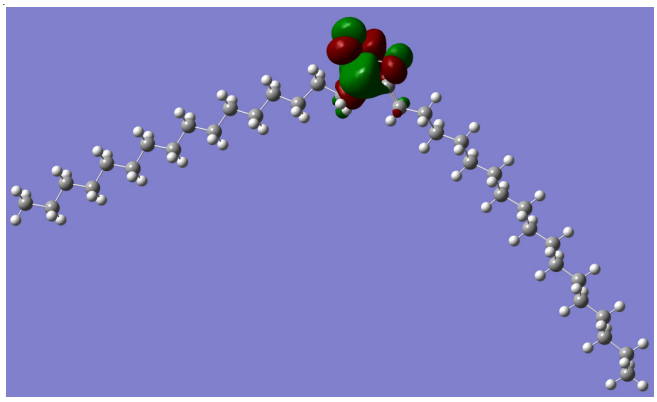

Fig. 4. LUMO

The reaction between molecules A and B, molecular frontier orbital theory presume that the HOMO electron of molecule A flow to the LUMO of molecule B and the the HOMO electron of molecule B flow to the LUMO of molecule A. Thus the flow of electrons caused the the formation and break down of chemical bonds. Only when the HOMO energy of molecules A (or B) closed to the LUMO energy of molecules B (or A), the flow between electrons can be easily occurred. Frontier orbital energy of ethanol is shown in Table-3. HOMO energy of ethanol close to the LUMO energy of alkyl ketene dimer.Therefore, the flow of electrons is prone to occur. As a nucleophile, ethanol can give electron. However, lactone ring of alkyl ketene dimer can obtain electronic in the reaction. In short, alkyl ketene dimer can react with ethanol.

TABLE-3
FRONTIER ORBITAL ENERGY OF ETHANOL (au)

	NHOMO	HOMO	LUMO	NLUMO
Orbital	12	13	14	15
Energy	-0.32507	-0.26845	0.03849	0.06857

Infrared spectra of alkyl ketene dimer and reaction product: In theory, the reaction products of alkyl ketene dimer and ethanol is shown in Fig. 5. Carbon atoms of carbonyl group is the active site. It can easily obtain electron. Therefore, the single bond between carbon and oxygen is broken down, As a result, β-keto esters is generated.

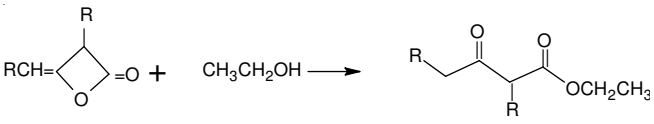

Fig. 5. Reaction products of alkyl ketene dimer and ethanol

The IR spectra of reaction product is shown in Fig. 6. The black (1) is infrared spectrum of the reaction product and the red (2) is infrared spectrum of alkyl ketene dimer. As can be seen from the figure, 1847 cm^{-1} (circle in the figure) is the characteristic peak of lactone ring. 1720 cm^{-1} is the absorption peak of C-O-C. After reaction, the characteristic peak of alkyl ketene dimer was disappeared, which indicate that ring-opening reaction of alkyl ketene dimer was occurred. 1635 cm^{-1} is characteristic absorption peak of β-keto esters, which can be verified that β-keto esters is generated.

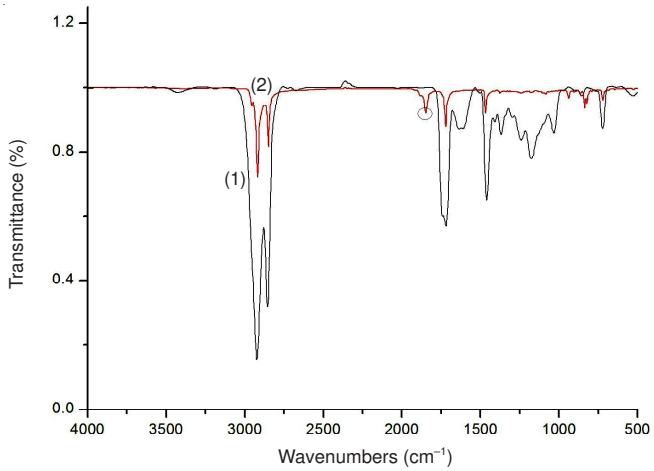

Fig. 6. IR spectrum

^{13}C NMR of alkyl ketene dimer and reaction product: Resonance position of aldehydes and ketones were in the lowest field. In general $\delta_C > 195$ ppm. In NMR spectra of alkyl ketene dimer, the signal at 169.781 ppm was lactones. The signal at 145.641 ppm belonged to unsaturatd carbon atom. However, in NMR spectra of modified alkyl ketene dimer 205.491 ppm was the peak of ketones. 169.991 ppm was the peak of esters. Obviously, alkyl ketene dimer react with ethanol and the product was β-keto esters.

SEM of sized paper: As can be seen from Figs. 7-10, paper without sizing, whose fiber array loose. The surface of body paper is rough, there is a large number of pores. However, a smooth film was formed in the surface of the sized paper, which covered the pores. Therefore, Water was difficult to penetrate the fiber interior. Although paper sized by melted modified-alkyl ketene dimer had covered the holes, the surface is rough compared with the paper sized by emulsion. The melted modified-alkyl ketene dimer was difficult to keep on the surface of body paper.

Cobb values were as shown in the Table-4. Body paper din not have water resistance. The Cobb value was 134.96 g/cm^2. The paper sized by surface sizing starch did not have water resistance too. Although the starch formed a film on the surface of the paper, the starch starch is a kind of absorbent material. The paper sized by alkyl ketene dimer emulsion had

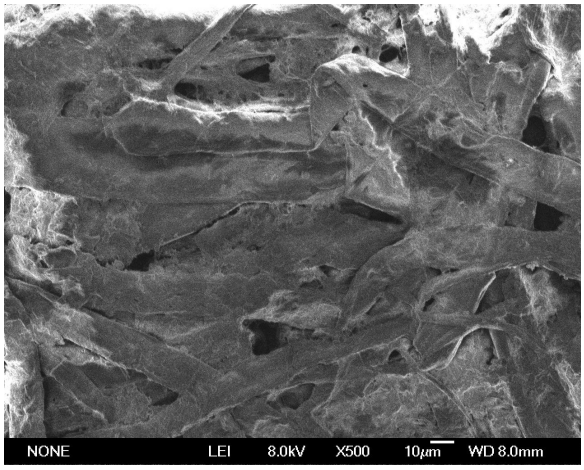

Fig. 7. Body paper

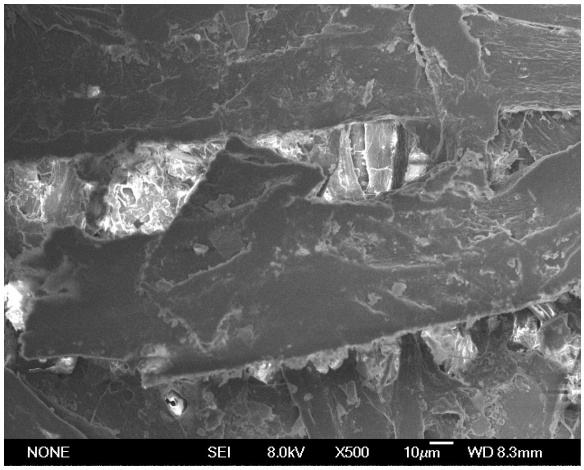

Fig. 8. Paper sized by modified-alkyl ketene dimer emulsion

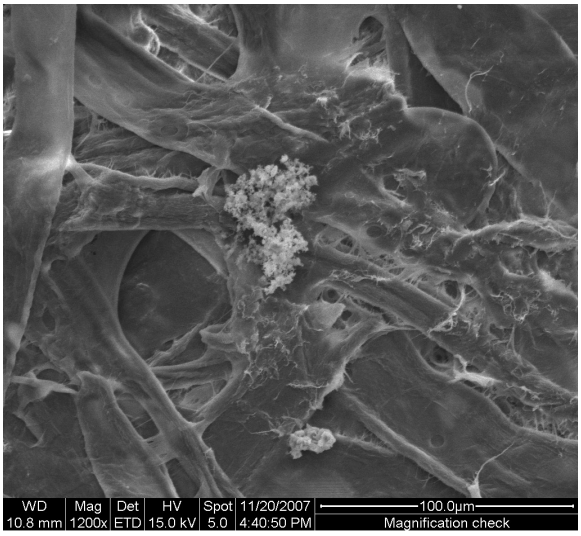

Fig. 9. Paper sized by alkyl ketene dimer emulsion

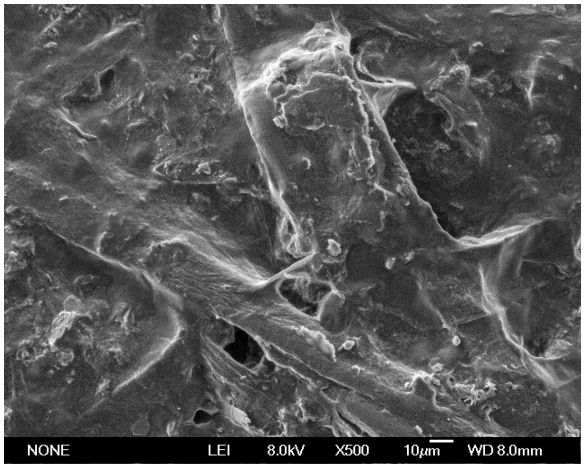

Fig. 10. Paper sized by melted modified-alkyl ketene dimer

the perfect water resistance.alkyl ketene dimer formed a film on the surface, which give the paper well water resistance. However, the paper sized by modified-alkyl ketene dimer emulsion possessed poor water resistance. But the Cobb value of the paper only sized by fused modified-alkyl ketene dimer was 6.51 g/cm^2, which indicate that the product of ethanol modified-alkyl ketene dimer possessed water resistance and the product of ethanol modified-alkyl ketene dimer was difficult to retain on the surface. So, it is believed that the reason why the paper sized by modified-alkyl ketene dimer emulsion did not have water resistance was that the modified-alkyl ketene dimer could not remain on the surface of paper.

TABLE-4
COBB VALUES

Number	Cobb value (g/cm^2)
(1)	134.96
(2)	22.59
(3)	92.36
(4)	6.51
(5)	129.89

PS: (1) body paper; (2) the paper sized by alkyl ketene dimer emulsion, surface sizing starch: alkyl ketene dimer emulsion =50:3; (3) the paper sized by modified- alkyl ketene dimer emulsion, surface sizing starch: modified- alkyl ketene dimer emulsion =50:3; (4) the paper only sized by fused modified- alkyl ketene dimer; (5) the paper only sized by surface sizing starch

Conclusion

Seen from the calculation results of Gaussian 03, reactivity of alkyl ketene dimer mainly concentrated in the lactone ring. Lactone ring can react with nucleophiles. By analyzing the IR spectra and ^{13}C NMR of the reaction product of alkyl ketene dimer and ethanol. nucleophilic reaction was proved. Therefore, we believe that alkyl ketene dimer can react with some substances contained hydroxyl and cellulose unit contains three hydroxyl groups, in theory, cellulose can also react with alkyl ketene dimer, which requires verification in later study.

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REFERENCES

1. X.-X. Qi and S.-M. Wang, *Chem. Ind. Times*, **12**, 30 (2005).
2. Z.-W. Han, *Chem. Technol.*, **5**, 29 (2005).
3. G. Garnier, M. Bertin and M. Smrckova, *Langmuir*, **22**, 7863 (1999).
4. S. Shibuichi, T. Onda, N. Satoh and K. Tsujii, *J. Phys. Chem.*, **100**, 19512 (1996).
5. R. Mohammadi, J. Wassink and A. Amirfazli, *Langmuir*, **22**, 9657 (2004).
6. T. Minami, H. Mayama and K. Tsujii, *J. Phys. Chem. B*, **112**, 14620 (2008).
7. W. Fang, H. Mayama and K. Tsujii, *J. Phys. Chem. B*, **111**, 564 (2007).
8. T. Onda, S. Shibuichi, N. Satoh and K. Tsujii, *Langmuir*, **9**, 2125 (1996).
9. G. Garnier and J. Wright, *Colloids Surf. A*, **145**, 153 (1998).
10. J.W. Davis, *Tappi J.*, **39**, 23 (1956).
11. R. Peter, *Tappi J.*, **68**, 83 (1985).
12. A. Isogai, *Nordic Pulp & Paper*, **7**, 193 (1992).
13. L.-G. Da, X. Bao and Y.-J. Wei, *J. Anqing Teachers College*, **1**, 122 (2010).
14. R.-B. Hou, *Univ. Chem.*, **5**, 29 (2010).
15. W. Zeng and Z.-D. Lin, *Comput. Appl. Chem.*, **2**, 205 (2008).