Study on Abrasion Resistance of UV Curing System

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Abstract

UV curing technology, with high efficiency, energy saving, environmental protection and other advantages, has rapidly developed into a new technology in digital imaging area. In order to avoid the printing graphic damaged during the circulation of printing press, the requirement of the rub resistance of UV curing system is higher and higher. Aiming to explore the rub resistance of UV-curable systems, different samples were prepared by changing the types and content of the prepolymer, reactive monomer and anti-abrasion, using the principles of the mass loss method abrasion meter test samples after curing wearable, analyze the effect of the variety and the content of prepolymer, reactive monomer and the type of wear-resistant additives on the rub resistance of UV-curable systems. The best abrasion UV curing system was determined by formulations experimental method. The results show that：The prepolymer and wear-resisting additives have great influence on the abrasion resistance of UV-curable systems. The active monomer, which can improve the rub resistance of the UV contribute to varnish, has certain influence on the UV-curable systems. The result is suitable for all the UV-curable systems, and it will contribute to the improvement of wear resistance of UV curing system.

Forewords

UV curing technology is caused by UV radiation curing resin, with fast curing, energy saving, room temperature curing, less pollution, coating superior performance advantages compared with other curing methods, in the digital printing industry has maintained rapid growth momentum. In order to avoid the printing graphic damaged during the circulation of printing press, the requirement of the rub resistance of UV curing system is higher and higher.

UV curing system mainly consists of the prepolymer, the reactive monomer, photoinitiator and additives etc. Under the UV radiation, photo-initiator is stimulated to become the free radical or the positive ion, and then it initiates the activated monomer and unsaturated double bond of the prepolymer to have the chemical reaction in the system and forms solidify with the structure of crossing linking. Monomer and prepolymer is an essential part of the UV curing system has a great influence on the rub resistance of Ink film. Wear while adding appropriate additives can improve ink performance, improve the rub resistance of UV curing system.

Experiment

Raw material

Prepolymer: Hyperbranched polyester acrylate A; Epoxy acrylate B; polyester acrylate C; Polyurethane acrylate D

Activated monomer: 2(2-Ethoxyethoxy) Ethylacrylate (EOEOEA); Headily diacrylate (HDDA); Tripropylene glycol diacrylate (TPGDA); Neopentyl glycol diacrylate (NPGDA); Trimethylol propane triacrylate (TMPTA); Propoxylated trimethylolpropane triacrylate (PO3-TMPTA)

Photoinitiator:1-Hydroxy-1-cyclohexyl-phenyl-ketone (184); Phenyl bis (2,4,6 - trimethylbenzoyl) phosphine oxide (819); 2 - methyl-1 - (4 - (methylthio) phenyl) -2 - morpholin-1 - propanone (907)

Rub resistance additives：EH-8025N; Talcum powder; SiO_2

Instrument

81-2 type constant temperature magnetic stirrer(Jiangsu jin fang city splendor equipment manufacture co ,LTD); UV light curing machine(FUSION, America); IGT F1 type printing eligibility(Netherlands IGT Reports B.V.); RKK303 multicoated Type of coating machine(RK England); Taber 5135 Abrasion tester(Taber America)

Preparation methods of ink

According to the UV curing system formulations, prepolymers, monomers, photo initiators and additives mixed according to a certain ratio, dispersion using an electric mixer with a magnetic stirrer dispersed, are ink samples.

Test method

Using the Taber abrasion tester to test abrasion resistance of tear sheet film layer and using Taber abrasion index to represent abrasion resistance. According to the formula (1) sample of taber abrasion index. Type of Iw as taber abrasion index; type of M_0 is the quality of the tear sheets before wear; M_r Is after abrasion proof of quality; r for the experiment of revolution.

$$Iw = (M_0 - M_r) \times 1000 / r \quad (1)$$

The results and analysis

Prepolymer on rub resistance of UV curing system

The prepolymer is the main film material in UV curing system, and has the greatest impact on the cured film properties. The other components of fixing UV curing system, choose four kinds of prepolymer to prepare 4 groups of varnish ink samples. Abrasion test four samples, the test results shown in Figure 1.

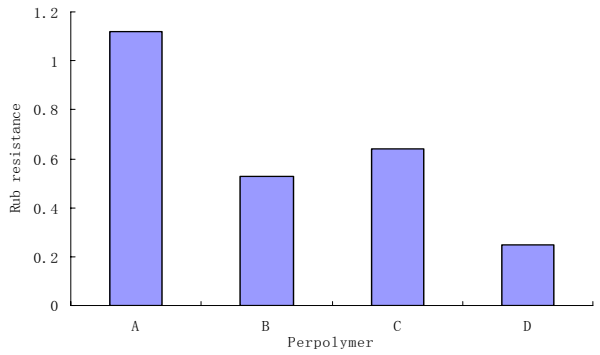

***Figure 1** prepolymer on rub resistance of UV curing system*

The figure 1 shows that types of prepolymer has great influence on rub resistance of the UV curing system. Aliphatic polyurethane prepolymers D, the best wear rub resistance of the sample prepared, B epoxy prepolymer samples prepared abrasion Secondly, hyperbranched polyester prepolymers A sample prepared wear worst. Because of Polyurethane acrylate EB270 contain large amounts of ammonia ester bond, it's easy to form hydrogen bond. When the stress is high, the hydrogen bond break absorbed energy, has protected the covalent bond; The external force rescission, re-formation of hydrogen bonds. So that the film showed excellent wear resistance. Epoxy prepolymer B main chain structure is rigid structure, hardness, but low tensile strength, easy to cause ink off to reduce wear. Hyperbranched polyester prepolymer molecule A branched multi-crosslinked or crosslinked network is too high for long enough missing in a soft segment, resulting in increased brittleness, in the external force is likely to cause stress concentration, stress can through the surrounding structure-borne dispersion, the film stress points brittle chipping off, so the wear resistance of the samples prepared worst. Polyester prepolymer C a lot of mechanical properties between epoxy acrylates and urethane acrylates, So the preparation of the sample of the abrasion resistance between prepolymer B and prepolymer D wear resistance between the sample preparation.

In order to obtain good wear resistance performance of the UV curing system, the choice of B and D in the prepolymer compound, Using two component simplex centroid design methods to determine the mix of the prepolymer component. Let x1, x 2, respectively prepolymer ratio of B and D, According to two component simplex centroid design method (m = 2), There are shown in Table 1 three types of formulations were prepared with three kinds of samples of formulation, performance test results are shown in Table 1.

Tab.1, Formulation experiment and results

NO.	X1 (B)	X2 (D)	Rub resistance
1	1	0	0.53
2	0	1	0.25
3	1/2	1/2	0.33

Through data processing, calculate the rub resistance indicators index membership and a composite score of each formulation. Since m = 2, so the regression equation of the form as follows:

$$y = b_1x_1 + b_2x_2 + b_1b_2x_1x_2 \quad (2)$$

The calculated integrated sub (y) and Table 2 x1, x2 values are substituted into equation (2), we obtain three equations, solving simultaneous equations can be obtained varnish rub resistance composite indicator regression equation:

$$y = 0.87x_2 + 2.25x_1x_2 \quad (3)$$

Using 10 recipes to the formula (3) verification experiments, the experimental and calculated values of the variance is 0.00056，the deviation is very small. Description experimental and predicted values corresponding curve fitting very well, the resulting formulation has a high credibility. Through solver can get, when x 1 = 0.31, x2 = 0.69, the regression equation to get the maximum extreme. Namely, when the rate of two kinds of prepolymer is B: D = 0.31:0.69, the rub resistance performance of the best sample. Samples were prepared according to the optimal formula to test its resistance to wear Iw = 0.23 sample good wear resistance.

Monomer effect on rub resistance of the UV curing system

The function of the active monomers is reactive diluent, crosslinking agent and strengthening agent performance, it also has important influence on the performance of the ink layer. Fixed UV curing system other components, the choice of seven kinds of monomers, preparation of 7 group of ink samples. Abrasion test four samples, the test results shown in Figure 2.

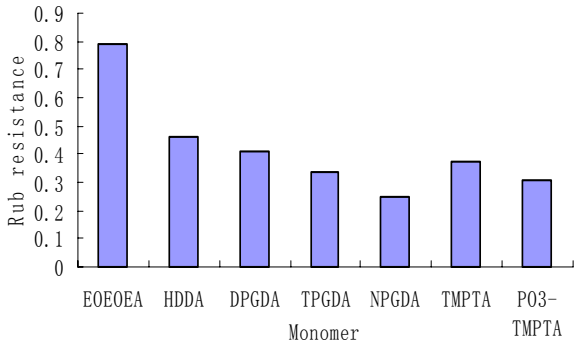

***Figure 2** Monomer effect on rub resistance of the UV curing system*

Figure 2 shows that with the increase of monomer functionality, the samples first increases and then wear a downward trend. TPGDA difunctional monomer is the best wear resistance of the sample preparation. EOEOEA monofunctional monomer because only one reactive group in the curing process can not produce crosslinking points, crosslinking density is low, resulting in decrease in abrasion resistance. For a multi-tube to monomer, the functional monomer increases as the coating crosslinking increases, the hardness is increased, which is advantageous to improve wear resistance; On the other hand, with

the increase in functionality, the curing shrinkage rate of the film increases, the adhesion to the substrate fall, cause the coating to flake off, wear value increases, abrasion resistance decreases.

Different monomers on the contribution of different ink properties, in order to obtain in order to obtain good rub resistance, the choice of the monomer TPGDA, NPGDA, PO3-TMPTA, the use of experimental design formula mixed monomer formulations. Let X1, X2, X3, respectively, TPGDA, NPGDA, PO3-TMPTA 3 monomers in the monomer mixture in the ratio of formulation, the rub resistance of each formulation as shown in Table 3.

Tab.2 Formulation experiment and results

NO.	X1	X2	X3	Rub resistance
1	1	0	0	0.51
2	0	1	0	0.90
3	0	0	1	0.61
4	1/2	1/2	0	0.32
5	1/2	0	1/2	0.57
6	0	1/2	1/2	0.56
7	1/3	1/3	1/3	1.62

Through data processing, calculate the rub resistance indicators index membership and a composite score of each formulation. Third-order three-factor simplex centroid design specifications and test indicator variable regression equation between, As shown in Equation (4).

$$\hat{y} = \sum_{i=1}^{3} b_i x_i + \sum_{i<j} b_{ij} x_i x_j + b_{123} x_1 x_2 x_3 \quad (4)$$

The integrated sub into the formula (4) is calculated regression coefficients and regression coefficients into the equation, to get integrated sub and regression equation between the variables, as shown in Equation (5) below.

$$y=0.86x_1+0.55x_2+0.78x_3+1.18x_1x_2-0.05x_1x_3+0.58x_2x_3-24.85x_1x_2x_3 \quad (5)$$

Using 10 recipes to the formula (5) verification experiments, the experimental and calculated values of the variance is 0.00035，the deviation is very small. Description experimental and predicted values corresponding curve fitting very well, the resulting formulation has a high credibility. By Solver, under our experimental conditions, the optimal composite monomer mass ratio TPGDA: NPGDA = 0.63:0.37, the sample optimum rub resistance. Samples were prepared according to the optimal formula to test its resistance to wear Iw = 0.21 sample good rub resistance.

The prepolymer and monomer ratio on the rub resistance of UV curing system

Prepolymer and monomer are the main materials constituting UV curing system. The ratio between them wear resistance to UV curing systems have a great impact. Other components of fixed UV curing system, change B, D prepolymer mixed with TPGDA, NPGDA ratio between the monomer mixture was prepared varnish samples, abrasion resistance test sample, the results shown in Figure 3.

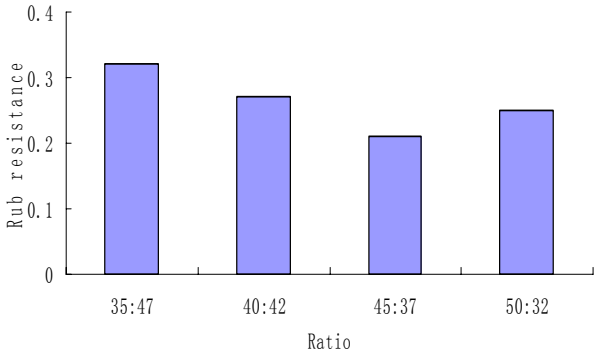

Figure 3 *The prepolymer and monomer ratio on the rub resistance of UV curing system*

Figure 3 shows that the wear resistance of the sample with the prepolymer and monomer ratio increases with the increase, but the proportion is too high, but reduced abrasion resistance. The reason is: polymeric material depends primarily on the strength of the main chain bond force and intermolecular force, increasing the strength of the main chain or to increase the intermolecular forces, the polymer can increase the strength. The prepolymer content increased, ink molecular weight increases, the ink layer strength and wear resistance are good; prepolymer content exceeds 45%, the increase in ink viscosity, is not conducive to ink leveling and wetting of the surface , the surface state is not good, the friction coefficient becomes large, abrasion resistance decreased. Prepolymer and monomer ratio of 45:36 at the best wear resistance of the sample.

Rub resistance additives on the impact of UV curing systems

The use of wear-resistant additives can effectively improve the strength of the ink layer and reduce the friction coefficient, the ink has better wear resistance. Other components of fixed UV curing system, the choice of three kinds of varnish wear additives Sample Preparation 3 groups, the control group had no additives added, the wear resistance of the test sample, shown in Figure 4.

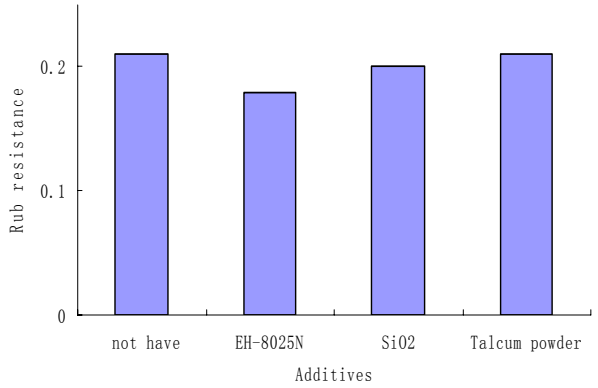

Figure 4 *Rub resistance additives on the impact of UV curing systems*

Figure 4 shows that, adding SiO_2, talc varnish wear compared with the control group did not change significantly, adding EH-8025N varnished improved wear resistance. EH-8025N main component is silicon fluorine compound nanotechnology, namely the small size of nanoparticles uniformly dispersed in the resin, the ink surface is smooth, the friction process of the ink film, the nanoparticles surface enrichment of the ink film, acts as a self-lubricating effect, reducing the friction coefficient of the ink; second ink resin on the surface is worn, the enrichment of the surface of nano-particles of silicon compound fluorine lubricating film is sufficient to form a complete, the resin is less likely to be worn small, and thus improved wear resistance.

The amount of wear additives to the UV curing system also affects the wear resistance, UV curing systems Fixed Fixed other components, wear additives to change the amount of EH-8025N, 5 sets of samples were prepared to test the wear resistance results shown in Figure 5.

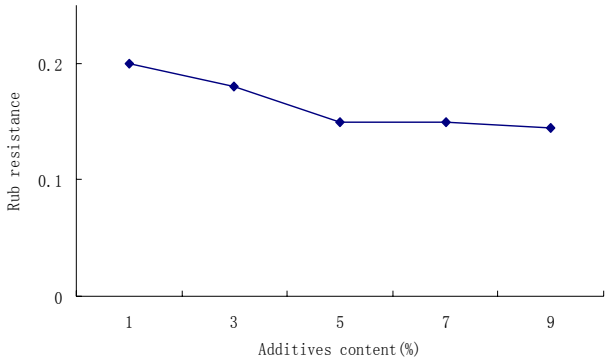

***Figure 5** Additive content on the rub resistance of UV curing systems*

As can be seen from Figure 5, with the amount of additives increases, the wear resistance increased gradually to 5% when the UV curing system, the best wear resistance, further increasing the amount of additives to improve the wear resistance can be seen change slowed. Wear additive is added to significantly improve the wear resistance of UV curing system, increasing the amount of wear additives, nanoparticles can provide a large surface area, but also can absorb a lot of molecular chain, so that substantially uniform stress distribution, reducing the local region by the frictional stress, improve wear resistance. But when the additive amount of more than 5%, the nano-particles into small aggregates starting group, and can not form a homogeneous phase system, nano-particles and a resin phase separation phenomenon occurs, resulting in no significant increase wear resistance of the ink layer.

Conclusions

(1) The type of the prepolymer prepared by UV curing system, the printing after the film there is a big difference in wear resistance of the polyurethane prepolymers prepared by UV curing system D has excellent wear resistance, the composite prepolymer UV curing system better wear resistance, when the prepolymer B: D is prepared at 0.31:0.69 UV curing system has good abrasion resistance.

(2) Preparation of different monomers, UV curing systems, printed after the film there is a big difference in wear resistance, with the increase of monomer functionality, UV curing system first increases and then wear a downward trend, two functional monomer is NPGDA best wear resistance of the sample preparation. Monomer mixture by TPGDA: NPGDA = 0.63:0.37 mixed UV curing system has good abrasion resistance.

(3) The ratio of prepolymer and monomer abrasion resistance to UV curing system to a certain extent, the prepolymer and monomer ratio of 45:36, UV curing system, the best wear resistance.

(4) The UV curing system, nano-technology-wear additive fluorosilicone compound EH-8025N, UV curing systems can effectively improve the wear resistance; additives reached 5% of the UV curing system, the best wear resistance.

References

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