Synthesis of (Solvent-Based) PU Composite as Coating Materials

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Abstract: As PU considered as one of unique polymer that achieve especial characteristics, Solvent based PU composite was investigated as a textile coating material, solubility,viscosity and fixation condition were studied, the study confirmed that the PU with concentration 30% achieved the best composite recipe with addition of 0.5% activator.
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Keywords: Synthesis; Solvent-Based; PU Composite; Coating Material

1. Introduction

In this study solvent-based PU were studied Solve polyurethane adhesives have been of great economical and technical importance because of their easy processing and high performance. They have been used traditionally for the bonding of rubber, leather, textiles, metal, paper, wood, and plastics including highly plasticized polyvinyl chloride.

These adhesives consist of high molecular weight (approximately 100,000) dissolved in a solvent. They are formed by the reaction of high molecular weight polyester diols with a diisocyanate. [(1)]as a coating materials, starting from dissolvetion until reaching the applicable recipes.

2. Materials & Chemicals

2.1. PU “polyurethane granules” HP1090AK (high molecular weight) (1), HP1090AK (medium molecular weight) (2) and HP1090AK (low molecular weight) (3), thermo-plast, headway advanced materials, Taiwan.

2.2. Primary solvent DMF “di methyl formamide”, MW 73.09 purity 99%.

2.3. Secondary solvent wetting agent 0S-406, Guanzhi chemical, china.

2.4. Thickening agent (silicon oxide nano-form powder), Clariant, Germany.

2.5. Blue oil-based pigment, SPI, Egypt.

3.6. Activator, Guanzhi chemical, china.

3. Tools and Equipment:

3.1. Silk screen manual machine.

3.2. Disperser.

3.3. Heat press with temperature and time control.

3.4. squeegee blade.

3.5. Roll mill.

3.6. Digital Rotational Viscometer.

4. Methodology

PU granules were dissolved into DMF with stirring for 30 min. using a high speed disperser (1500 rpm), then wetting agent was added to the mixture with continuous stirring for 10 min., the mixture then milled using roll-mill laboratory machine until homogenous paste was obtained, the prepared paste was pigmented using 5% of blue oil-based pigment 100PC, the prepared paste was applied onto various types of fabric, after washed out the colour fastness and physical properties for all coated samples were studied.

The pigmented samples were subjected to colour fastness tests and fixation study, while the clear samples were subjected to physical tests.

5. Procedures

5.1. Solubility Study

5.1.1. Studying the solubility of PU granules DMF solvent

Three types of the thermo-plast polyurethane granules, PU (1) high molecular, PU (2) medium molecular, PU (3) low molecular were tested. 50 gm. from each type of PU granules were dissolved into 50 gm. of the solvent DMF (Ratio 1:1) with shaking for 3 hours. [(2)]The results observed and reported in Table (1).

1% from wetting agent was added to each recipe, the result observed and reported in Table (1).

5.2. Studying the effect of wetting agent onto PU-DMF coating film.

Wetting agent was added in a percentages of (0.5%, 1%, 1.5%, 2%, 2.5%), to a composite with ratio composed of (50/50 PU/DMF), the 5 samples were left for about 3 hours, results observed and reported in Table (2).

Table (1): Solubility of PU

	DMF	DMF + Wetting agent
Concentration	99%	99 % + 100%
Temperature	At room temp.	At room temp.
Time	3 hours	3 hours
PU1	I	I
PU2	I	I
PU3	I	S
I = Insoluble S= Soluble		

Table (2): Effect of wetting agent into solubility of TPU

Temperature	At room temp.				
Time	3 hours				
Wetting agent concentration	0.5%	1%	1.5%	2%	2.5%
TPU/DMF (50%/50%)	PS	PS	S	S	S
S= Soluble					
PS= Partially Soluble					

5.3. Studying the applicable ratios of PU/DMF as a coating material.

Five ratios of PU granules and DMF solvent were prepared as reported in Table (3) with addition of 1.5% of wetting agent. Thickening agent (silicon oxide nano-form powder) also added to low viscous paste to be applicable, the viscosity was measured for all ratios, results were reported in Table (4) (5) and Fig. (1).

6. Fixation study

6.1. Studying the fixation temperature onto different ratios (PU/DMF) coating film:

Five coated samples of PU with concentration (25%, 30%, 40%, 50%, and 60%) were fixed at different temperature (60**,** 80, 100, 120, 150, 170, 180, 200) ^{0}C for 20 sec. by using heat press, after fixation, the samples washed out at 40 ^{0}C for 10 min. by non-ionic detergent 5gm/L and rinse it 5 min. at 40 ^{0}C and rinse it 5 min. on running cold water.

After drying, all samples were subjected to colour reader for measuring total colour difference (ΔE) before and after washing, all results were reported in Table (6) and illustrated figures (2), (3), (4), (5) and (6).

Table (3): Studying different ratios between PU/DMF

PU Granules (%)	25	30	40	50	60
DMF (%)	75	70	60	50	40
Wetting agent (%)	1.5%				

Table (4): Viscosity of different ratios between PU/DMF on coating paste

Coating Paste					
PU Granules (%)	25	30	40	50	60
DMF (%)	75	70	60	50	40
Viscosity (CP)	245	505	1736	3945	4970
Silk screen print (observation)	N/A	N/A	N/A	A	H/A
N/A = Not Applicable A = Applicable H/A= Hard Applicable					

Table (5): Viscosity after adding more thickener of different ratios between PU/DMF on coating paste

Coating paste			
PU Granules (%)	25	30	40
DMF (%)	75	70	60
Thickener (%)	6	5	2
Viscosity (CP)	3951	3947	3950

Table (6) Studying fixation temperature onto different ratios (PU/DMF) coating film

PU/DMF paste	Total Colour Difference (ΔE)							
	60^0C	80^0C	100^0C	120^0C	150^0C	170^0C	180^0C	200^0C
(25/75)%	34.43	33.68	32.35	31.49	12.21	9.77	9.34	4.23
(30/70)%	22.37	21	19.59	7.87	4.14	3.76	2.66	1.96
(40/60)%	5.88	4.76	4.34	3.99	3.50	2.88	2.70	1.45
(50/50)%	8.99	6.63	6	5.90	3.30	4.49	7.76	9.89
(60/40)%	9.07	8.42	6.10	6	4.14	6.04	10.67	11.79

Paste composition: PU (HP1090AK)/DMF Coating Paste 950 gm., Blue solvent-based pigment 50gm

6.2 Studying the fixation time onto the different ratios (PU/DMF) coating film.

Five coated samples of PU with concentration (25%, 30%, 40%, 50%, and 60%) were fixed at different time (10, 20, 30, 40, 50, and 60) second.

For PU concentration of (25%, 30%, 40%) the fixation temperature was at 200 ^0C while for PU concentration of (50% and 60%) the fixation temperature was at 150 ^0C.

After fixation all samples washed out at 40 ^0C for 10 min. by non-ionic detergent 5gm/L and rinse it 5 min. at 40 ^0C and rinse it 5 min. on running cold water, After drying, all samples were subjected to colour reader for measuring total colour difference (ΔE) before and after washing, all results were reported in Table (7) and illustrated Figures (7), (8), (9), (10), and (11).

Table (7): Studying the fixation time onto the different ratios (PU/DMF) coating film

PU/DMF paste	Total Colour Difference (ΔE)					
	10sec.	**20sec.**	**30sec.**	**40sec.**	**50sec.**	**60sec.**
(25/75)% at 200 ^0C	9.17	4.33	2.23	2.69	1.94	1.90
(30/70)% at 200^0C	2.70	1.66	1.50	1.45	1.30	1.20
(40/60)% at 200^0C	2.66	1.60	1.55	1.49	1.30	1.25
(50/50)% at 150^0C	5.95	3.15	3	3.10	3.98	4.06
(60/40)% at 150 ^0C	6.09	4.10	3.99	4.05	4.20	5.12

6.3. Studying the fixation temperature onto different ratios of (PU/DMF) coating film with addition of 0.5% activator:

Five samples PU paste (25%, 30%, 40%, 50%, and 60%) with addition of 0.5% catalyst to each sample were fixed at different temperature (60, 80, 100, 120, 150, 170, 180, 200) ^0C for 20 seconds by using heat press, after fixation all the samples washed out at 40 ^0C for 10 min. by non-ionic detergent 5gm/L and rinse it 5 min. at 40 ^0C and rinse it 5 min. on running cold water.

After drying, all samples were subjected to colour reader for measuring total colour difference (ΔE) before and after washing, all results were reported in Table (8) and illustrated Figures (12), (13), (14), (15) and (16).

Table (8) Studying the fixation temperature onto different ratios of (PU/DMF) coating film with addition of 0.5% activator

PU/DMF paste	Total Colour Difference (AE)							
	60^0C	80^0C	100^0C	120^0C	150^0C	170^0C	180^0C	200^0C
(25/75)%	10.90	9.80	7.50	5.90	4.89	2.73	1.78	1.68
(30/70)%	2.70	2.65	2.60	2.57	1.96	1.68	1.25	1.05
(40/60)%	3.90	3.85	3.77	3.55	3.03	2.83	2.38	1.13
(50/50)%	6.44	6.31	5.77	5.61	3.10	3.37	3.60	4.05
(60/40)%	6.99	6.89	5.86	5.69	3.64	4.54	4.66	5

Paste composition: PU (HP1090AK)/DMF Coating Paste 950 gm., Blue oil-based pigment 50gm., Activator 5gm.

3.4. Studying the fixation time onto the different ratios (PU/DMF) coating film with addition of 0.5% activator.

Five samples PU paste with concentration of (25%, 30%, 40%, 50%, and 60%) with addition of 0.5% catalyst to each sample were fixed at different time (10, 20, 30, 40, 50, 60) Sec.

For PU concentration of (25%, 30%, 40%) the fixation temperature was at 180 ^0C while for PU concentration of (50% and 60%) the fixation temperature was at 150 ^{0}C.

After fixation all samples washed out at 40 ^{0}C for 10 min. by non-ionic detergent 5gm/L and rinse it 5 min. at 40 ^{0}C and rinse it 5 min. on running cold water, After drying, all samples were subjected to colour reader for measuring total colour difference (ΔE) before and after washing, all results were reported in Table (9) and illustrated Figures (17), (18), (19), (20) and (21).

Table (9) Studying the fixation time onto the different ratios (PU/DMF) coating film with addition of 0.5% activator.

PU/DMF paste	Total Colour Difference (ΔE)					
	10sec.	20sec.	30 sec.	40sec.	50sec.	60sec.
(25/75)% at 180^{0}C	1.71	1.69	1.28	1.22	1.19	1.15
(30/70)% at 180^{0}C	1.35	1.30	1.25	1.20	1.15	1.02
(40/60)% at 180^{0}C	1.80	1.56	1.30	1.24	1.17	1.10
(50/50)% at 150^{0}C	2.72	2.70	1.66	1.25	1.70	2.50
(60/40)% at 150^{0}C	3.29	3.20	2.10	1.30	1.91	2.94

4. Confirmation test:

A confirmation sample of PU/DMF with recipe of (30%,70%) respectively in addition of 0.5% catalyst prepared as mentioned at methodology with addition 5% of Thickening agent (silicon oxide nano-form powder) to adjust viscosity for screen application.

After drying all samples were subjected to colour reader for measuring total colour difference (ΔE) before and after washing out, all results were reported in Table (10).

Table (10) ΔE before & after washing out for (30%PU, 70%DMF) coating films for various fabric

Fabric		100% Cotton	(50%Cotton & 50%polyester)	100% Polyester
(30/70)%PU/DMF	ΔE	1.30	1.28	1.27

Fixation condition: at 180^{0}C for 30 Sec.

4. Discussion:

Solubility Study:

Tables (1) and (2) showed that PU 3 was dissolved well while PU2 and PU 3 not dissolved and the solubility of PU3 was improved with addition of 1.5% wetting agent.

Viscosity study:

1.2. Studying the applicable ratios of PU/DMF as a coating material.

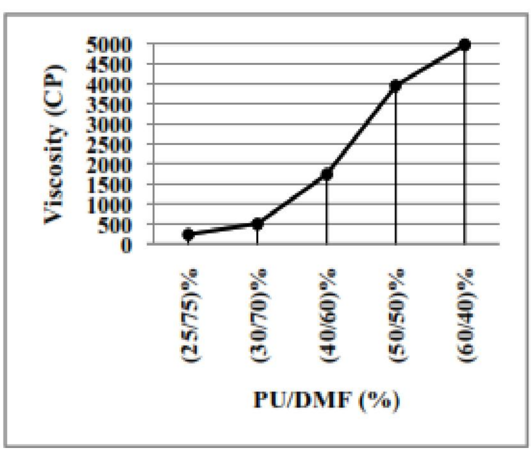

Fig. (1) Relation between PU/DMF Concentration and viscosity.

Tables no. 4, 5 and illustrated Figure (1) Showing that the viscosity increased as the percentage of PU granules increased, as 25% showing the lower viscosity value 245 CP, while 60% PU showing the higher value of viscosity 4970 CP. [3]

As the percentage of 25%, 30%, 40% PU still showing low viscosity, more Thickening agent was recommended to achieve applicable viscosity, 6%, 5%, 2% thickener respectively was the best percentage as cleared at Table no. 5

Fixation study

2.1. Studying the fixation temperature onto different ratios (PU/DMF) coating film:

Table no.6 and illustrated Figures (2), (3), (4), (5), (6) showed that the total color difference ΔE was decreased with the increase of temperature, the best fixation result was at 200 ^{0}C for the first three samples (25%, 30%, 40%) while after 150 cracking was noticed at the last two samples (50%, 60%), from figures found that the total colour difference (ΔE) decreased as the percentage of PU increased to reach 40% after that recipe total colour difference (ΔE) increased at same curing temperature from 60^0**C** until 200^0**C**. [4] [5] [6]

The best fixation result obtained at 200^{0}C for recipes (25%, 30%, 40%) while 150^{0}C for recipes (50%, 60%).

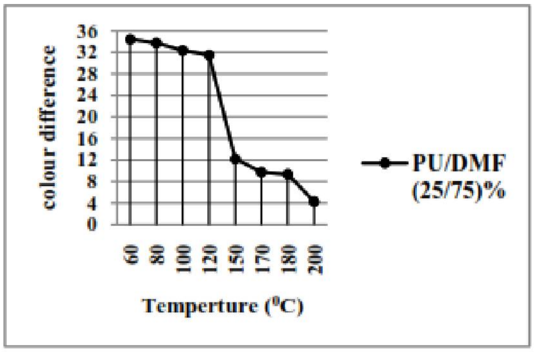

Fig. (2): Relation between fixation temperature & ΔE onto (25%,75%) PU/DMF

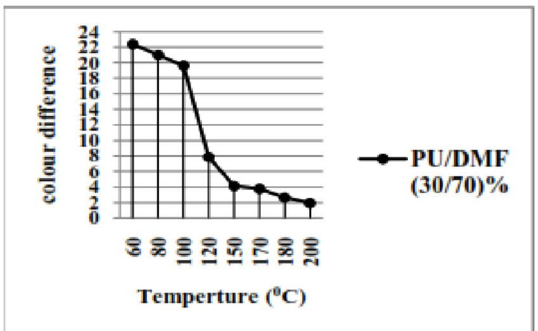

Fig. (3): Relation between fixation temperature & ΔE onto (30%,70%) PU/DMF

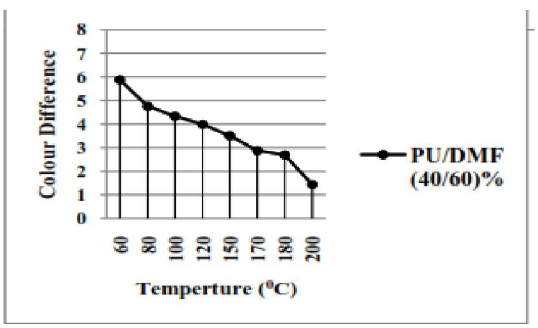

Fig. (4): Relation between fixation temperature & ΔE onto (40%,60%) PU/DMF

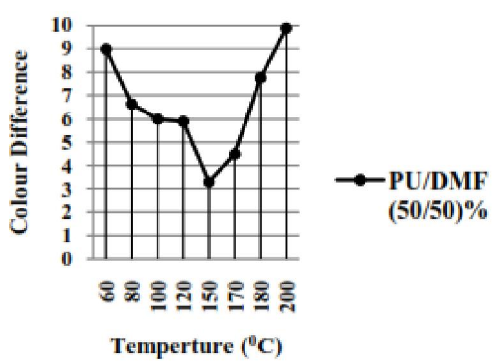

Fig. (5): Relation between fixation temperature & ΔE onto (50%/50%) PU/DMF

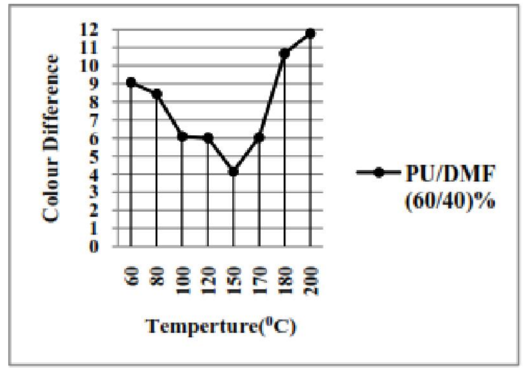

Fig. (6): Relation between fixation temperature & ΔE onto (60%/40%) PU/DMF

Table (8) and figures (12), (13), (14), (15), (16). showed that after addition of 0.5 activator the ΔE improved as good results were achieved at 180^{0}C for recipes (25%, 30%, 40%) and 150^{0}C for recipes (50% and 60%) without affecting the background of the fabric. [(7) (8)]

Studying the fixation time onto the different ratios (PU/DMF) coating film.

Table (7) Figures (7), (8), (9) declared that recipes of PU 25%, 30%, 40% showing a decrease of total colour difference Δ E with theincrease of fixation time, while for recipes 50%, 60% Δ E decrease gradually when increasing fixation time reach 30 Sec. and increasing again for fixation time 40, 50, 60 Sec. Because cracking occurred.

Figures (10), (11) declared that if at fixation time more than 30 sec. a reversible action occurred as ΔE value increased with the increase of fixation time due to cracking occurred.

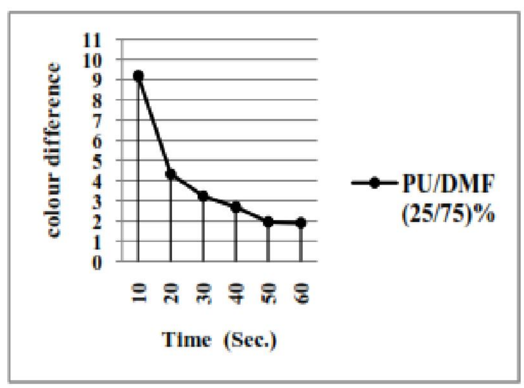

Fig. (7): Relation between fixation time & ΔE onto (25%,75%) PU/DMF coating at 200^{0}C

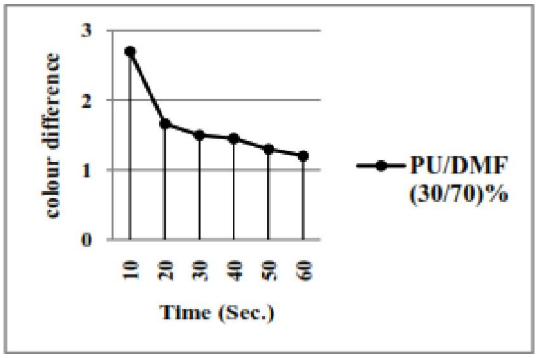

Fig. (8): Relation between fixation time & ΔE onto (30%,70%) PU/DMF coating at 200^{0}C

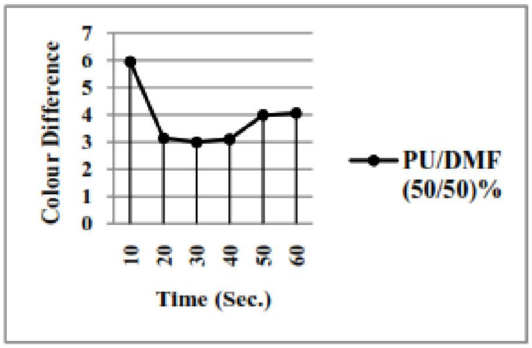

Fig. (9): Relation between fixation time & ΔE onto (40%,60%) PU/DMF coating at 200^{0}C

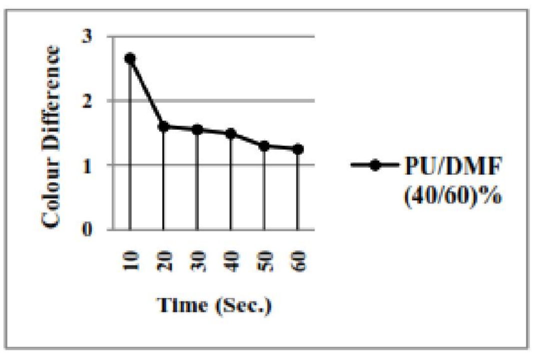

Fig. (10): Relation between fixation time & ΔE onto (50%,50%) PU/DMF coating at 150^{0}C

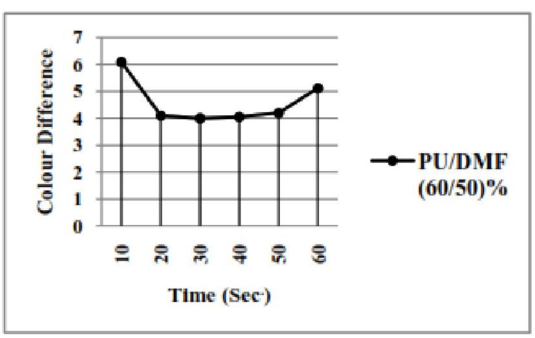

Fig. (11): Relation between fixation time & ΔE onto (60%/40%) PU/DMF coating at 150^{0}C

From table (9) and figures (17), (18), (19), (20), (21) showed that:

The best curing time for PU concentration (25%, 30%, 40%) after addition of.5% activator at180 ^{0}C was 60sec. while for PU concentration (50%,60%) the best curing time at 150 ^{0}C was 30sec. above this point yellowing of fabric background was noticed.

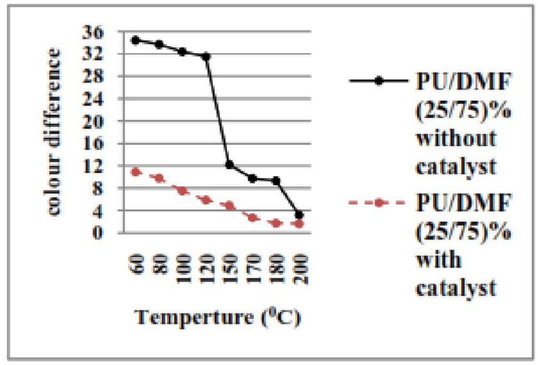

Fig. (12): Relation between fixation temperature & ΔE onto (25%75%) PU/DMF before & after activator

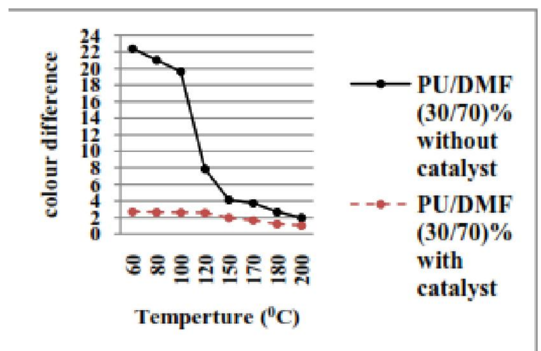

Fig. (13): Relation between fixation temperature & ΔE onto (30%,70%) PU/DMF before & after activator

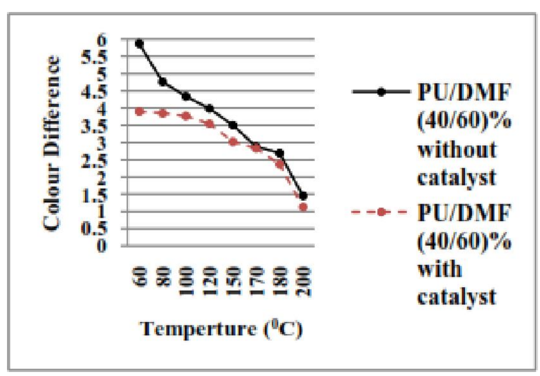

Fig. (14): Relation between fixation temperature & ΔE onto (40%,60%) PU/DMF before & after activator

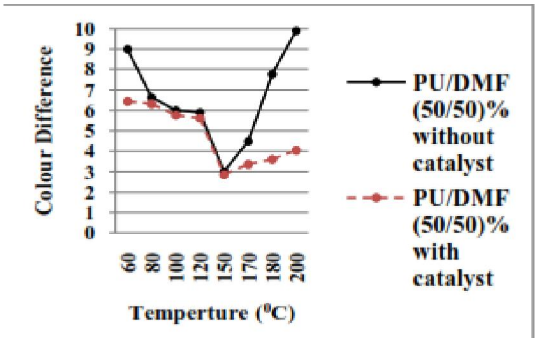

Fig. (15): Relation between fixation temperature & ΔE onto (50%/50%) PU/DMF before & after activator

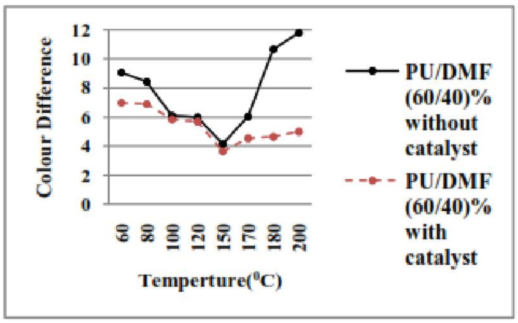

Fig. (16): Relation between fixation temperature & ΔE onto (60%/40%) PU/DMF before & after activator

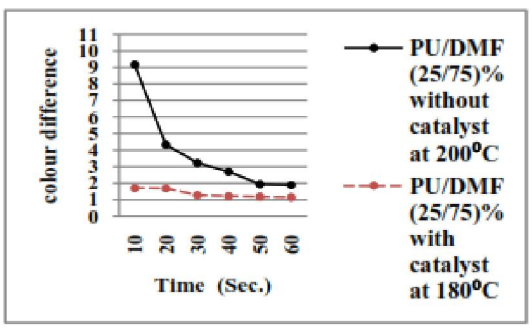

Fig. (17): Relation between fixation time & ΔE onto (25%,75%) PU/DMF

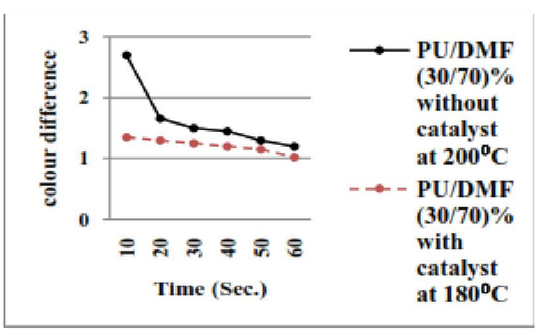

Fig. (18): Relation between fixation time & ΔE onto (30%,70%) PU/DMF

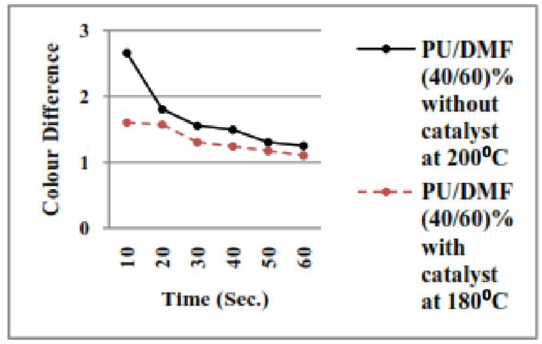

Fig. (19): Relation between fixation time & ΔE onto (40%,60%) PU/DMF paste

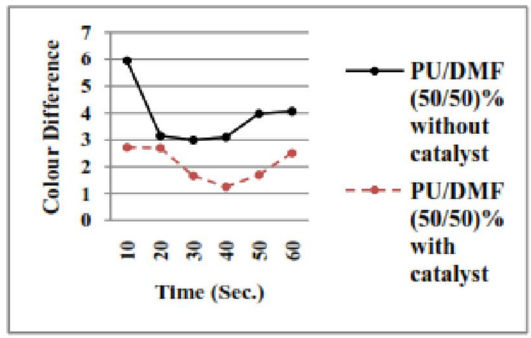

Fig. (20): Relation between fixation time & ΔE onto (50%,50%) PU/DMF at 150^{0}C

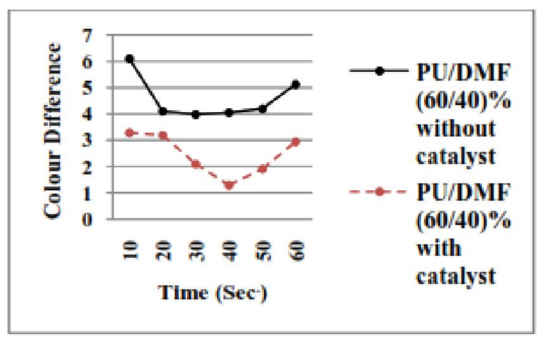

Fig. (21): Relation between fixation time & ΔE onto (60%, 40%) PU/DMF at 150^{0}C

Confirmation test:

From previous results a composite of PU concentration of 30% showed an excellent result of total colour difference ΔE at (180^{0}C for 30 sec.)

A confirmation test was done at the best fixation conditions (180^{0}C for 30 sec.) onto 100%Cotton, 50%/50% Cotton/Polyester Blend and 100% Polyester fabrics with the prepared composite of 30% PU concentration, ΔE achieved values of 1.30, 1.28, and 1.27 respectively, as reported in Table (10).

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