

CHAPTER 11

Experimental

2.1 Materials and Instruments

2.1.1 Materials

Chemical compounds used in the experiments were listed below .

Table 2.1 List of chemicals.

Name	Mol.wt.	Source	Grade
1) Tributyltin Oxide	596.08	ITRI	R.G.
2) Methacrylic Acid	86.09	SCI	R.G.
3) Acrylic Acid	72.06	SCI	R.G.
4) Methyl Methacrylate	100.12	Fluka	R.G.
5) tertiary-Butyl Acrylate	128.17	Fluka	R.G.
6) Benzoyl Peroxide	242.23	BHD	A.R.
7) Sodium Hydroxide	40.00	Merck	A.R.
8) Sodium Sulfate	142.04	Merck	A.R.
9) Molecular Sieve Type 4 A ^o	-	Union carbide	
10) Toluene	92.15	Merck	A.R.
11) Petroleum ether	-	BHD	A.R.
12) Acetone	58.08	Local	R.G.

Name	Mol.wt.	Source	Grade
13) Methanol	32.04	Local	R.G.
14) Chlorinated Rubber	-	OSC	R.G.
15) Hydrochloric Acid conc.	36.46	Merck	A.R.
16) Sulfuric Acid conc.	98.08	Merck	A.R.
17) Nitric Acid Fuming	63.01	Merck	A.R.
18) Chloroform	119.38	Merck	R.G.
19) Xylene	106.17	Merck	R.G.
20) Calcium chloride Anhydrous	110.99	Fluka	R.G.
21) Stannous Chloride Standard		Merck	A.A.

Note : ITRI = International Tin Research Institute, London

SCI = Siam Chemical Industry Co., Ltd. Thailand

OSC = Oriental Siam Co., Ltd. Thailand

AA = For Atomic Absorption Analysis

Butyl = n-Butyl

2.1.2 Instruments

- : IR-Spectrophotometer, Perkin-Elmer, model Perkin-Elmer 780
- : Fourier-transform NMR Spectrometer, Jeol, model JNX-FX 90 Q
- : ^{119m}Sn Mossbauer Spectrometer, Cryophysics ltd., Oxford
with 512-channels data store, ITRI., England
- : Atomic Absorption Spectrophotometer Model AA-670, Shimazu
- : Elemental Analyzer, Perkin-Elmer, model Perkin-Elmer 240
CHNO Analyzer, Osaka university, Japan.

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- : Differential Scanning Calorimeter; DSC , DUPONT 9900 Thermal Analyzer driving 910 DSC cell, KRICT., Korea
- : Gel-Permeation Chromatography (GPC) Analyzer model WATERS 150-C ALC/GPC, KRICT., Korea
- : BK-6 Drying Recorder, six track, SHEEN INSTRUMENTS Ltd.,
- : Film Applicators. model REF. 1107 which gives 4 different film thicknesses of 30-60-90-120 mm, SHEEN INSTRUMENTS Ltd.,
- : Cross Hatch Cutter with six cutting edges 1 mm apart and 30 ° edge, BS 3900 : ASTM D3002 : DIN 53 151, SHEEN INSTRUMENTS Ltd.
- : Vacuum Oven : TOWNSON & MERCER LTD. Croydon, England
- : Eyela Aspirator A-2S : Tokyo Rikakikai Co., Ltd.
- : Eyela Cool Ace : Tokyo Rikakikai Co., Ltd.
- : Voltac VB-5 Variable V. Transformer
- : Gallenkamp SS 420 Mechanical Stirrer
- : Oil Bath and Water Bath
- : Micrometer film thickness, positest " Banana " Gauge, thickness range 0-200 um, SHEEN INSTRUMENTS Ltd.

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2.2 Purification of Materials

Purification of Methyl methacrylate (MMA) (19)

The purchased monomer, MMA, was purified by washing twice with 5 % aqueous NaOH to remove the inhibitor followed by washing several times with distilled water until neutral. It was then dried with sodium sulfate and distilled under reduced pressure to prevent polymerization in the fractionating column. The monomer was stored overnight under nitrogen in a refrigerator and used the following day.

Purification of Tertiary-butyl acrylate (t-BA)

The monomer was washed repeatedly with 5 % aqueous NaOH to remove inhibitors then with distilled water until neutral. Dried with CaCl_2 and sodium sulfate and distilled under reduced pressure. Then, sealed under nitrogen and stored at 0°C in the dark until used.

Purification of Methacrylic acid and Acrylic acid

Methacrylic acid was saturated with NaCl (to remove the bulk of water) then the organic phase was separated and dried with CaCl_2 and distilled under vacuum.

2.3 Preparation of Organotin Monomers

The tri-n-butyltin methacrylate and tri-n-butyltin acrylate monomers were prepared according to the method of Montermoso et.al. (20)

Tri-n-butyltin methacrylate (TBTM)

To a solution of 103.80 (0.174 mole) of bis(tri-n-butyltin)oxide in 300 ml of toluene in 1 l. three necked flask fitted with a dropping funnel, a mechanical stirrer and a condenser, was added slowly 30.00 g (0.348 mole) of methacrylic acid while cooling to below 25°C. The mixture was azeotropically distilled under reduced pressure and stirred. The reaction temperature and pressure was adjusted to allow the mixture to reflux at 30°C for 4 hr., at the end of which 3.1 ml of water was collected. Toluene was evaporated in a rotary evaporator while keeping the temperature of the solution below 30°C. The viscous liquid residue was diluted with 150 ml of petroleum ether and cooled to -20°C. The mixture was kept at this temperature for 2 hr. and the long transparent crystals was collected by filtration to give 117.356 g (~90 %) of TBTM. Tin content (Sn) was found to be 31.5 %.

Anal. calcd. for (C₁₆H₃₂O₂Sn) : C, 51.23; H, 8.60; Sn, 31.64

Found : C, 51.74; H, 8.60; Sn, 31.50

IR (KBr) max cm⁻¹ : 2980-2860 (C-H, str, alkane), 1640 (C=C, str, alkene), 1620 (C=O, str, -COOSn(Bu)₃), 1420 (C-H bending, CH₂), 1370 (C-C, bending), 1200-1180 (C-O-C, str, ester), 1205 (C-Sn, bending).

¹H NMR of TBTM (CDCl₃) δ ppm : 0.91-1.07 (m, 9H, -CH₃), 1.35-1.65 (m, 18H, -CH₂), 1.94 (s, 3H, CH₂=C-CH₃), 5.48-6.05 (d, 2H, CH₂=C(CH₃)₂).

^{13}C NMR of TBTM (CDCl_3) δ ppm : 13.75 ($-\text{CH}_3$), 16.54 ($-\text{CH}_2$), 19.04 ($\text{CH}_3-\text{C}=\text{O}$), 28.78-27.07 ($-\text{CH}_2-\text{Sn}$), 124.45 ($\text{CH}_2=\text{C}$), 137.98 ($\text{CH}_2=\text{C}(\text{CH}_3)_2$).

Tri-n-butyltin acrylate (TBTA)

A 25.1 g (0.348 mole) of acrylic acid and 103.8 g (0.174 mole) of bis (tri-n-butyltin)oxide were dissolved in 300 ml of toluene. The solution was heated to reflux at atmospheric pressure. Refluxing was continued for 4 hr., at the end of which, 3.0 ml of water had been collected in the azeotropic distillation head. Toluene solvent was removed with the aid of a rotary evaporator and the resulting product was purified by crystallization from petroleum ether. The tri-n-butyltin acrylate monomer separated out as needlelike crystals having a melting point of 74-74.5°C. The yield of the monomer was 119.25 g (~95%). Tin content (Sn) in the monomer was 32.7%.

Anal. calcd. for ($\text{C}_{15}\text{H}_{30}\text{O}_2\text{Sn}$) : C, 49.90; H, 8.37; Sn, 32.87

Found : C, 50.38; H, 8.67; Sn, 32.70

IR (KBr) ν max cm^{-1} : 2980-2850 (C-H, str, alkane), 1640 (C=C, str, alkene), 1580 (C=O, str, $-\text{COOSn}(\text{Bu})_3$), 1420-1410 ($=\text{CH}_2$, bending), 1370 (C-C, asym), 1280 (C-O, str, ester), 1205 (C-Sn, asym).

^1H NMR (CDCl_3) δ ppm : 0.97 (m, 9H, 3X- CH_3), 1.28-1.51 (m, 18H, 9X- CH_2), 5.65-5.78 (m, $\text{CH}_2=\text{CH}-\text{C}=\text{O}$), 6.15-6.24 (m, $\text{CH}_2=\text{CH}-\text{C}=\text{O}$)

^{13}C NMR (CDCl_3) δ ppm : 13.65 ($-\text{CH}_3$), 16.52 ($-\text{CH}_2-\text{Sn}$), 27.84 ($-\text{CH}_2-$), 129.26 ($\text{CH}_2=\text{CH}-\text{C}=\text{O}$), 130.40 ($\text{CH}_2=\text{CH}-\text{C}=\text{O}$), 171.45 (C=O)

2.4 Preparation of Homopolymers

2.4.1 Preparation of Organotin Homopolymers (21)

Organotin monomers; TBTM and TBTA were prepared and purified by the same procedure previously described. Each homopolymer was prepared by solution polymerization in toluene (3 mol/l) in the presence of benzoyl peroxide (BPO) initiator with a concentration of 1 mole % by wt. of monomer. The solution was flushed with oxygen-free nitrogen and heated in a thermostatically controlled water bath at $75 \pm 1^\circ\text{C}$ for 7 hr. At the end of the reaction, the polymers were collected and purified by reprecipitation from 90 % methanol-water mixture several times. The precipitated polymers were dried in vacuum oven at 30°C for 24 hours and weighed.

Anal. calcd. for poly TBTM ($\text{C}_{16}\text{H}_{32}\text{O}_2\text{Sn}$) : C, 51.23; H, 8.60; Sn, 31.64

Found : C, 51.66; H, 8.60; Sn, 31.47

Anal. calcd. for poly TBTA ($\text{C}_{15}\text{H}_{30}\text{O}_2\text{Sn}$) : C, 49.90; H, 8.37; Sn, 32.87

Found : C, 50.17; H, 8.40; Sn, 32.60

IR (KBr) ν max cm^{-1} : 2990-2850 (C-H, str, alkane), 1645 (C=O, str, $-\text{COOSnBu}_3$), 1370 (C-C, bending), 1220-1170 (C-O-C, str, ester), 1250 (C-Sn, bending)

^1H NMR (CDCl_3) δ ppm : 0.92-0.98 ($-\text{CH}_3$), 1.28 ($-\text{CH}_2$)

^{13}C NMR (CDCl_3) δ ppm : 13.76 ($-\text{CH}_3$), 16.09 ($-\text{CH}_2-\text{Sn}$), 27.08 - 28.01 ($-\text{CH}_2-$), 180.31 (C=O).

2.4.2 Preparation of Poly MMA and Poly t-BA

Polymerization of MMA and t-BA were carried out using solution polymerisation at the same condition as for the preparation of copolymers. Predetermined amounts of each monomer was dissolved in toluene (3 mole/l) using benzoyl peroxide as initiator (1 mole % by wt. of monomer).

At the end of the reaction, Poly MMA as well as Poly t-BA was precipitated by pouring the reaction mixture into about eight times its volume of methanol. The precipitate was then dried in vacuum oven at 50°C for 24 hours. The yield of Poly MMA and Poly t-BA was found to be 87.7 and 90 % respectively. Tg of poly MMA and poly t-BA are 105 and 47.4 °C respectively.

IR (KBr) ν max cm^{-1} : (2980-2985, C-H, str, alkane), (1725, C=O, str, ester)
 The ^1H NMR spectrum of poly MMA shows the signals δ ppm : 1.63-1.84 ($\text{CH}_3\text{-C}(\text{CH}_2)\text{-C=O}$), 2.35 ($\text{CH}_3\text{-C}(\text{CH}_2)\text{-C=O}$), 3.60 ($\text{CH}_3\text{-OC=O}$)

IR (KBr) ν max cm^{-1} : (2980-2985, C-H, str, alkane), (1730, C=O, str, ester)
 The ^1H NMR (CDCl_3) of poly t-BA δ ppm : 1.44 ($(\text{CH}_3)_3\text{C-O}$), 1.82 ($\text{CH}_2\text{-CH-C=O}$) and 2.18 (CH-C=O).

^{13}C NMR (CDCl_3) of poly t-BA δ ppm : 28.06 ($(\text{CH}_3)_3\text{C-O}$), 42.43 ($\text{CH}_2\text{-CH-C=O}$), 80.34 ($(\text{CH}_3)_3\text{C-O}$), 174.17 (C=O).

2.5 Preparation of Copolymers

The copolymers were obtained by solution polymerization using benzoyl peroxide as a free-radical initiator and toluene as solvent. The concentration of total monomers in the reaction mixture were 3 mole /l . The composition of the copolymer obtained was calculated by elemental analysis and by determining tin content via oxidation of the sample to tin oxide. The ratios of monomers in the initial reaction mixture were varied over a wide range and the corresponding compositions of the copolymers formed were determined.

2.5.1 Copolymerization of Tri-n-butyltin methacrylate with Methyl methacrylate and with Tertiary-butyl acrylate.

Predetermined amounts of monomers were dissolved in toluene (3 mole/l) using benzoyl peroxide as initiator (1 mole % of monomer). The solutions were flushed with oxygen-free nitrogen and heated in an oil bath maintained at $75 \pm 1^\circ\text{C}$ for 7 hours. The polymers were collected and purified in methanol-water mixture (90:10), dried and weighed.

The yields of organotin polymers were over 85 % in all cases. The initial monomers mixture and polymer compositions for each reaction were given in table 2.2.

^1H NMR (CDCl_3) of TBTM-MMA δ ppm : 0.92 ($-\text{CH}_3$), 1.29 ($-\text{CH}_2$), 1.93 ($\text{CH}_3-\text{C}=\text{O}$, in MMA), 3.56 ($\text{CH}_3-\text{O}-\text{C}=\text{O}$, in MMA)

^{13}C NMR (CDCl_3) of TBTM-MMA δ ppm : 13.73 ($-\text{CH}_3$), 16.14 ($-\text{CH}_2-\text{Sn}$), 27.09-28.08 ($-\text{CH}_2-$), 51.63 ($\text{CH}_3-\text{OC}=\text{O}$), 178.85 ($\text{C}=\text{O}$ in MMA), 183.49 ($\text{C}=\text{O}$, in TBTM)

^1H NMR (CDCl_3) of TBTM-t-BA δ ppm : 0.91-0.97 ($-\text{CH}_3$), 1.28 ($-\text{CH}_2$), 1.43 ($(\text{CH}_3)_3\text{C}-\text{O}$)

^{13}C NMR (CDCl_3) of TBTM-t-BA δ ppm : 13.71 ($-\text{CH}_3$), 16.25 ($-\text{CH}_2-\text{Sn}$), 27.33 - 27.95 ($-\text{CH}_2$), 45.45 ($\text{CH}_2-\text{CH}-\text{C}=\text{O}$), 79.85 ($(\text{CH}_3)_3\text{C}-\text{O}$), 178.34 ($\text{C}=\text{O}$, in t-BA), 183.55 ($\text{C}=\text{O}$, in TBTM)

2.5.2 Copolymerization of Tri-n-butyltin acrylate with Methyl methacrylate and with Tertiary-butyl acrylate

The procedure was the same as above, but the copolymerization temperature was increased to 80°C .

^1H NMR (CDCl_3) of TBTA-MMA δ ppm : 0.91-0.98 ($-\text{CH}_3$), 1.29 ($-\text{CH}_2$), 1.45 - 1.63 ($\text{CH}_3-\text{C}-\text{C}=\text{O}$, in MMA), 3.59 (CH_3-O)

^{13}C NMR (CDCl_3) of TBTA-MMA δ ppm : 13.71 ($-\text{CH}_3$), 16.36 ($-\text{CH}_2-\text{Sn}$), 27.09 - 27.85 ($-\text{CH}_2$), 44.59 ($-\text{CH}-\text{C}=\text{O}$), 51.74 ($\text{CH}_3-\text{OC}=\text{O}$), 177.80 ($\text{C}=\text{O}$ in MMA), 180.89 ($\text{C}=\text{O}$, in TBTA)

^1H NMR (CDCl_3) of TBTA-t-BA δ ppm : 0.90-0.97 ($-\text{CH}_3$), 1.43 ($(\text{CH}_3)_3\text{C}-\text{O}$), 2.31 ($\text{CH}-\text{C}=\text{O}$)

^{13}C NMR (CDCl_3) of TBTA-t-BA δ ppm : 13.71-14.41 ($-\text{CH}_3$), 16.41 (CH_2-Sn), 27.09 - 28.15 ($-\text{CH}_2$), 42.04 ($-\text{CH}-\text{C}$), 80.23 ($(\text{CH}_3)_3\text{C}-\text{O}$), 174.12 ($\text{C}=\text{O}$, in t-BA), 180.04 ($\text{C}=\text{O}$, in TBTA)

Table 2.2 Proportions by mole of the reactants used for preparation of copolymers

composition of the feed monomers (mole/mole)			
TBTM:MMA	TBTM:ter-BA	TBTA:MMA	TBTA:ter-BA
0.08:0.02	0.08:0.02	0.08:0.02	0.08:0.02
0.06:0.04	0.06:0.04	0.06:0.04	0.06:0.04
0.05:0.05	0.05:0.05	0.05:0.05	0.05:0.05
0.04:0.06	0.04:0.06	0.04:0.06	0.04:0.06
0.03:0.07	0.03:0.07	0.03:0.07	0.03:0.07
0.02:0.08	0.02:0.08	0.02:0.08	0.02:0.08

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2.6 Characterization of Monomers and Polymers

2.6.1 ^{119m}Sn Moessbauer Spectra

The technic of Mossbauer spectroscopy was used to study the tiny changes in the nuclear-energy levels of tin arising from hyperfine interactions with its electronic environment. The isomer shift, is a shift of the centre of the Moessbauer absorption spectra resulting from the electrostatic interaction between the nuclear charge and the s-electron density. This parameter is particularly sensitive to change in bonding. (30)

The spectra were obtained by using a constant-acceleration spectrometer, the symmetrical triangular velocity-drive waveform being derived from the multichannel analyzer driven in the time mode by an external crystal-controlled oscillator; 512 channels were used throughout. A 15-mCi Ca ¹¹⁹SnO₂ source was used at room temperature, and the samples were packed in perapex discs and cooled to 80 k by using a continuous-flow cryostat with helium-exchange gas. The spectrometer was calibrated by using the magnetic splitting of an enriched Fe absorber foil. The data were folded to determine the zero-velocity position and the folded data fitted with lorentzian functions by a least-squares-fitting programme. The nonlinearity of the spectrometer was determined, by a free fit of the Fe data, to be less than 0.06 %, the quoted experimental error of 0.02 mm/sec in the measured values of isomer shifts takes into account errors associated with non-linearities, calibration, zero-velocity determination, and computer-fitting.

2.6.2 Infrared (IR) Measurement

Infrared Spectra of monomers ; TBTM, TBTA, MMA, t-BA and organotin copolymers were recorded using Perkin-Elmer Infrared Spectrophotometer model 780. As TBTM monomer was liquid, neat technique was used. The TBTA monomer was solid crystal so it was examined by a pressed-disc technic using KBr cell. For polymer samples, they were prepared by thin film technic.

2.6.3 Nuclear Magnetic Resonance (NMR) Measurement

The ^1H and ^{13}C NMR spectra of monomers and polymers were taken by using Fourier transform NMR spectrometer, Jeol, model JNX-FX 90 Q. The samples were dissolved as 5 % solution in CDCl_3 .

2.6.4 Molecular Weight Determination

Molecular weight characterization of the polymers was made by gel permeation chromatography (GPC) analysis, using 500 \AA - 100 \AA ultra-styragel columns from Water Associates Co., Ltd.

The polymers were dissolved in a tetrahydrofuran solvent and the eluting solvent was tetrahydrofuran at a flow rate of 1 ml/min. Refractive Index Detection was used. The samples concentration was 0.5 wt. % and 150 μl injection. The data in this thesis showed number-average and weight-average molecular weight and also molecular

weight distribution of polymers. Only some mole ratio of polymers were determined in this case.

2.6.5 Glass Transition Temperature (T_g)

Glass Transition Temperature and DSC thermograms of polymers were obtained over the temperature range -100° to 200°C and 0° - 250°C using Du Pont DSC Thermal analyser model 9900 driving 910 DSC Cell. The heating rate of $10^{\circ}\text{C}/\text{min}$, the N_2 (g) flow rate of 30 ml/min and the sensitivity setting of 0.2 and 0.5 were used. Specimens were punched out from a polymer sheet. The weight of specimens used was 10.0-25.0 mg. To obtain reliable T_g of the polymers, each of them was run twice in the above range of temperatures.

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2.7 Analysis of copolymer compositions.

2.7.1 Determination of Tin in Copolymers

A. Principle

The polymer is decomposed by wet-ashing with mixed $H_2SO_4-HNO_3$, and tin is determined in its inorganic form either volumetrically, photometrically or by Atomic absorption spectroscopy (A.A.S) (22). For this study, the A.A.S. technic was used.

B. Method (23)

The sample ca. 200 mg. was transferred to a suitable beaker and 10-20 ml of H_2SO_4 (conc.) was added and then HNO_3 (conc.) was added dropwise (~ 20 drops at the first stage) and warmed, if necessary, to start the reaction. The addition of HNO_3 was continued so that an excess acid (denoted by copious brown fumes) was always present. Eventually the beaker was placed on the hot plate and wet-ashing was continued until all the organic matter was decomposed and a colourless or pale yellow solution was obtained. Then 20 ml distilled water was added, boiled and evaporated to fume again. The solution was then colourless. If it was not, additional ~ 1 ml HNO_3 and ~ 0.5 ml $HClO_4$ was added and heated to H_2SO_4 fume again. The digestion of polymers took about 24 hr. to complete. For the determination of tin by A.A.S care must be taken that the H_2SO_4 concentration was the same in all samples including the standards. (24)

C. Preparation of standard solutions for plotting the tin calibration curves

Stannous chloride standard solution, 1,000 ppm for AAS ,(75 ml) was pipetted into a 250 ml volumetric flask, and double distilled water was added to bring the volume up to 250 ml. The stock solution concentration became 300 ppm. The stock solution (50 ml) was pipetted into four volumetric flasks and diluted with distilled water to a final concentrations of 50,100,150 and 200 ppm . The concentrations of standard solutions for calibration curves were 50, 100, 150, 200 and 300 ppm. λ max of tin was 286.3 .

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2.8 Polymer Film Testing

2.8.1 Preparation of Varnish

The polymer varnishes were prepared from (50 % by wt.) of polymer solutions using xylene as a solvent.

2.8.2 Preparation of Standard Panels for Varnish Testing

Steel panels for testing were of rust-free flattened mild steel in sheet or strip form and showed a minimum of surface roughness and discoloration. The surface roughness should not exceed 1.5 μm . This would be accomplished with burnishing operation. It was carried out by dry rubbing using grade 220 silicon carbide paper. The panels were burnished uniformly and a suitable sequence of operations were as follows: (25)

1. the panel was straight across in a direction parallel to any one side.
2. All signs of the original burnishing had been removed at right angles to the first direction .
3. With a circular motion of diameter approximately 80-100 mm, until a pattern had been produced consisting only of circular burnishing marks superimposed one upon another. The burnished panels before use were cleaned. The surface of the finally cleaned panels were not touched by hand or otherwise contaminated. If the varnishes coating could not be applied immediately, the cleaned panels should be stored in a desiccator.

2.8.3 Measurement of Film Thickness

Control of film thickness is an important part of paint testing. Film thickness measurements are a check or other associated tests in the laboratory, on the skill and will of the painters, and on the performance of automatic painting machinery.

A number of methods for measuring film thickness are available. The choice depends on where the film is located (laboratory or field). The substrate (wood, metal, plaster etc.) on the surface texture of the substrate (smooth or rough or flat or wavy) and whether the film is wet or dry.

For this thesis, dry film thickness was determined. There are many methods used for measuring dry film thickness, but only a few are suitable for all types of species and circumstances. Some require removal of the film from the substrate and thereby destroy or damage the film; others make small holes in the film but, in some instance, may be considered nondestructive; a large number depend on magnetic or electrical functions and are nondestructive. Naturally, these types are limited to metallic substrates, specifically ferromagnetic metals for the magnetic method.

In the thesis, a microgauge is somewhat easier to manipulate. A balanced beam is attached to the shaft of a light-duty motor spring. At the end of one arm is the magnet, which is counterbalanced by a rider on the other arm. The free end of the spring is attached to a ring. Rotation of the ring raises or lowers the magnet. In the determination the gage is placed on the specimen and is held firmly

with the thumb of one hand on the housing near the magnet; with the thumb or finger of the free hand, the ring is rotated counterclockwise to bring the magnet into contact with the specimen; the ring is then rotated clockwise until the magnet breaks loose. The thickness was read on the scale on the rim of the ring.






2.8.4 Cross-Cut Test (26)

This method of test specifies an empirical test procedure for assessing the performance of a coating of a paint, varnish or related product by measuring a property which depends, among other factors, on the adhesion of the coating to the substrate. After prepared the varnish coated test panel (in accordance with BS 3,900 part A₃ and A₄), the coated test panels should be dried for 24 hr. the procedure for cross-cut are as follow:

- a. The cutting tool face was held in a plane normal to the test panel surface.
- b. The 6 cuts were made with uniform pressure on the cutting tool in the coating in an even, non-jerky manner and at a cutting rate of 20 mm/s to 50 mm/s. All the cuts were penetrated through to the surface of the substrate but should not cut too deeply into the latter.
- c. This operation was repeated making further parallel cuts of equal number, crossing the original cuts and at 90° to them so that a lattice pattern was formed.
- d. A standard cellophane adhesive tape was covered on the lattice pattern. Be sure there was no void between the adhesive tape and the film. Finally took out the tape rapidly in the direction close to 180°.

The evaluation was done by examining the cut surface of the test coating, using normal vision. Corrected if necessary and classify it according to table 2.4 by comparing with the descriptions using illustrations as a guide. In general, the first three steps (in table 2.3) will normally suffice for general purposes and shall be used where a "go / no go" assessment was required.

TABLE 2.3 Classification of test results

Classification	Description	Appearance of surface or cross-cut area from which flaking has occurred (example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not distinctly greater than 5 % is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area distinctly greater than 5 %, but not distinctly greater than 15 % is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area distinctly greater than 15 %, but not distinctly greater than 35 % is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area distinctly greater than 35 %, but not distinctly greater than 65 % is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	

2.8.5 Drying Time Test (27)

The instrument required here was "Drying recorders" model BK-6 from Sheen Instruments Co.,Ltd. The technic for preparing test strips and for reading the results were :

1. The required speed was selected by turning the speed control knob in a clockwise direction and sliding in or pulling out to the required speed. Released the knob.
2. Film polymer was applied about 37 um width, from the prepared varnish to the test strips and placed them on the recorder.
3. The release lever was lifted on the back of the needle carrier and slided it to the starting position.
4. The needles were lowered on to the test strips.
5. On switched and the needles would now commenced the run along the strips..On reaching the end of the travel the carrier automatically stopped. Switched of.
6. Individual glass strips might be removed from the machine simply by depressing one end of the strip so that the opposite end lifted clear of the holder.

The recorder defines stages in the drying process as the first. stage was a pear-shaped impression corresponding to the time taken for evaporation of sovent. The second stage was the cutting of a continuous track corresponding to a sol-gel transition. The third stage was an interrupted track corresponding to the surface-dry time. And the last stage was where the needle no longer penetrates the film; corresponding to the final drying time.

In this test method, the track operated over a period of 12 hr. Observation of the film streak was done during and after those period. (12 hr.). The evaluation was by examining whether the streak on the film was presented or not. If it was absent along 12 hr., assessment for drying time property of that polymer film was passed.



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