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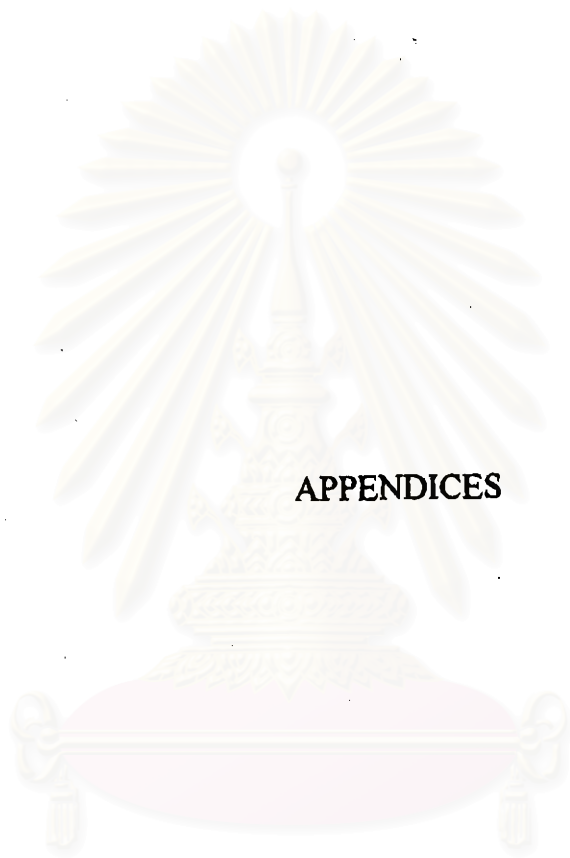
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APPENDICES

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Specification of Raw Materials

Table A1 Specification of polymeric MDI (Raypol C900) supplied by Thai Polyurethane Industry Co., Ltd.

Specifications	Polymeric MDI (Raypol C900)
Physical state at room temperature	Liquid
Color	Fawn to dark brown
Odor	None to aromatic at room temperature
Density at 25°C (g/ml)	1.24
Viscosity at 25°C (cps)	200-500
% Free NCO (by weight)	31.5
Flash point (°C)	>200
Crystallization temperature (°C)	<10
Shelf life at 20 °C (month)	6
Average functionality	2.7

The polymeric MDI and polyester polyol were melted and preheated to 70-80 °C, and degassed under vacuum for at least 30 minutes until any vigorous foaming and bubbling ceases.

Table A2 Specification of polyester polyol (F113) supplied by Thai Polyurethane Industry Co., Ltd.

Specification	Polyester polyol (F113)
Acid number (mg KOH/g)	0.5-0.8
Hydroxyl number (mg KOH/g)	54-58
Viscosity at 60°C (cps)	1,050-1,200
Color (APHA)	<100
Water content (%)	<0.05
Density at 25°C (g/cm)	1.16

Table A3 Specification of 1,4-BD supplied by Thai Polyurethane Industry Co., Ltd.

Specifications	BDO
Boiling point at 760 mm.Hg abs.(°C)	229.5
Boiling range (°C)	2
Specific gravity at 20 °C	1.01541
Refractive index at 20 °C	1.446
Flash point (°C)	134
Viscosity at 20 (°C)	90-92
Hydroxy value	1230
Acid value	0
Freezing point (°C)	19.3-19.5
Water content (%)	<0.2

Table A4 Specification of styrene monomer supplied by Siam Polystyrene Co., Ltd.

Specifications	Styrene monomer
Molecular weight	104.14
Inhibitor	<i>para-tert</i> -butylcatechol (< 0.01%)
Form	Liquid
Color	Colorless
Odor	Strong penetrating aromatic hydrocarbon
Boiling point (°F)	293
Freezing point (°F)	-23
Specific gravity (H ₂ O) at 77 °F	0.901
Vapor pressure at 68 °F (mmHg)	5
Soluble in	Ethyl alcohol, ethyl ether, carbon disulfide, methanol and acetone
Flash point (°F)	88

A trace of hydroquinone in styrene monomer was removed by washing with 1.0 % NaOH solution followed by washing with distilled water and then dried with anhydrous Na₂SO₄. The dried styrene monomer was distilled under reduced pressure and stored under nitrogen atmosphere at 5-10 °C.

Calculations [2-3]

1 Equivalent weight

The equivalent weight of a molecule is its molecular weight divided by the number of reactive groups available.

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Number of reactive groups or functionality}}$$

2 Percentage Free NCO

The amount of NCO available in a pure or impure mixture of diisocyanates for reaction is the percentage free NCO

$$\% \text{ NCO} = \frac{\text{Molecular weight of NCO}}{\text{Molecular weight of MDI}}$$

Polyols and polymeric isocyanates are often used whose molecular weight and functionality are not known and in these instances their equivalent molecular weights are determined by isocyanate (NCO) or hydroxyl (OH) group analysis.

3 Equivalent Weight of an Isocyanate

Many of the commercial reactants used in urethane synthesis are impure materials, for example MDI may be used as pure MDI, a low melting-point (38°C) solid; polymeric or 'crude' MDI, which is a dark-coloured low viscosity liquid. Also, active isocyanate content of a prepolymer decreases with storage, a decrease of about 0.05% per month being normal. For these reasons it is necessary to measure and specify the amount of isocyanate available for reaction at any specific time, and this is done by calculation of the isocyanate equivalent weight of the mixture using the following procedure:

Molecular weight of NCO group = % available (free) NCO

Equivalent weight of the reactant

$$\frac{42}{\text{Equivalent weight of the reactant}} = \% \text{ NCO}$$

Equivalent weight of the reactant

$$\frac{42}{\% \text{ available (free) NCO}} = \text{Equivalent weight of the reactant}$$

% available (free) NCO

4 Hydroxy Content

Polyols are identified by their hydroxyl numbers. Hydroxyl number is defined as the number of milliequivalents (or milligrams) of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer.

$$\text{Hydroxyl number} = \frac{56,100}{\text{Equivalent weight}}$$

Note: 56,100 is the molecular weight of potassium hydroxide (KOH) used in the analyses expressed in milligrams, i.e. KOH, 39.1+16+1 = 56.1, 56.1 x 1,000 = 56,100.

If the analysis of polyol indicates that the hydroxyl number is 48.3, then

$$\text{Equivalent weight} = \frac{56,100}{48.3} = 1,162$$

Note:

$$\text{Hydroxyl number} = \frac{(\text{Functionality}) (56,100)}{\text{MW polyol}} = \frac{56,100}{(\text{MW polyol})/(\text{Functionality})}$$

5 Isocyanate Index

The amount of isocyanate used relative to the theoretical equivalent amount, is known as the Isocyanate index.

$$\text{NCO index} = \frac{\text{Isocyanate equivalents}}{\text{polyol equivalents}}$$

Note: Normally excess isocyanate is used to compensate for allophanate and biuret readings.

As the chemical reaction on a 1:1 equivalent weight basis, the polyol would react with the polymeric MDI. This 1:1 equivalent weight is called the isocyanate index.

Characterization of Crosslinking Agent and Polyurethane Elastomers

1 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Model ACF200 Fourier-transform NMR Spectrometer. The chemical shift (δ) reported are given in part per million.

2 Tensile Testing (ASTM D638)

Tensile testing was performed by use of Instron Model 4301. The cross head speed of Instron tensile testing at 500 mm./min. was used. The median of five specimen was taken as the characteristic of the material tested. The load at rupture was recorded and divided by the original area of cross-section to express tensile strength in N/mm^2 using the following equation:

$$\text{Tensile strength} = F/A$$

$$F = \text{Tensile force (N)}$$

$$A = \text{Cross-section area (mm}^2\text{)}$$

The elongation at break or the ultimate elongation is the maximum extension of the specimen at the point of rupture.

$$\text{Elongation at break (\%)} = [(L-L_0)/L_0] \times 100$$

where $L-L_0$ = Change of length

L_0 = Original length

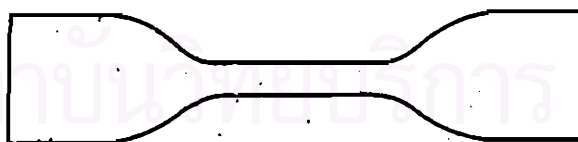
L = Final length at the point of rupture.

The plot of stress against strain yields the modulus of elasticity. This is the initial, straight-line portion of the stress-strain curve.

Stress-strain curves can also provide information on toughness of a material. An integration of the area under stress-strain curve is proportional to the energy-to-break per unit volume, which is a measure of the toughness of the specimen under the conditions of the test.

Preparation of Test Specimen

Polyurethane was cured in a mold of cavity size 50 mm X 150 mm X 3 mm (WxLxH). The specimen was cut by plastic sample cutting machine (Yasuda Seiki No. 189 PAL).



The tensile test specimen

Polyurethane, containing hydrophilic groups such as amino groups and polyoxyethylene segments, have reduced secondary intermolecular bonding when the amount of water vapour present in the atmosphere is high. The

physical properties as measured change significantly with humidity and specimen for testing must be allowed to reach equilibrium with a standard atmosphere at conditions :

$$23\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$$

$$50\% \pm 5\% \text{ relative humidity (R.H.)}$$

Thus, the specimen was conditioned for at least 3 hours at the above standard conditions.

Specimen of polyurethanes for tensile testing are produced by moulding in sheet form and cut by a puncher by mean of dies in dumbbell shape.

Thickness was then measured by a thickness micrometer. Three measurements of thickness were taken and the median value was used for calculating the cross-section area. Width of specimen is considered to be the width of the die used.

3 Dynamic Mechanical Analysis (DMA)

The dynamic response of a material to oscillatory loading, often sinusoidal wave, is usually carried out using a Dynamic Mechanical Analyzer. A sinusoidal stress is applied to a viscoelastic polymer. Its response correspondent to sinusoidal strain is out-of-phase behind the applied stress. Figure 3.4 shows the sinusoidal stress (σ) with the sinusoidal strain response (ϵ), and the lagging phase angle (δ).

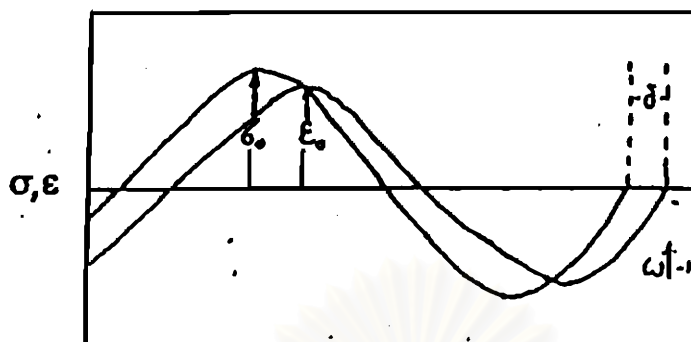


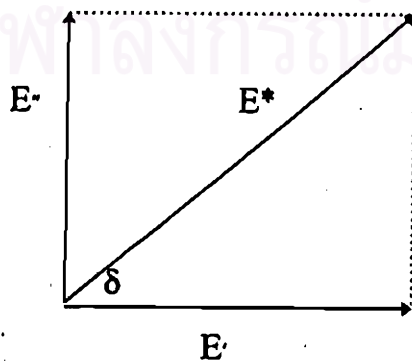
Figure 1 Sinusoidal stress with the strain response.

A complex modulus, E^* , is defined by σ_0 / ϵ_0 with the real and imaginary components, E' and E'' , which are also named respectively as the storage and loss modulus.

$$E^* = \sigma_0 / \epsilon_0$$

$$E^* = E' + E''$$

The relationship between these quantities is summarised in the Argand diagram shown below.



The ratio of the energy lost to the energy stored per deformation cycle, i.e., E''/E' or $\tan \delta$, is the most useful parameter. It exhibits peaks over a wide range of temperature. Each peak corresponds to a specific relaxation process, e.g., primary T_g (or $\alpha-T_g$) of the measured polymer.

In the present work, Netzsch DMA242 with the compression/penetration mode was used. The maximum force of 4.0 N was applied to sample with the frequency of 1.0 Hz. and the amplitude of 120 μm . The temperature was varied from -70 to 200 $^{\circ}\text{C}$, the heating rate was 5.0 K/min..

4 Thermogravimetric Analysis (TGA)

TGA is a technique used to measure the mass change with respect to a known total mass of determined material while the temperature is increased at constant rate. Weight losses occur when volatiles absorbed by the polymer are driven off, and at higher temperatures when degradation of the polymer occurs with the formation of volatile products.

In this work, Perkin Elmer TGA 7 was used. The heating rate was 20 $^{\circ}\text{C}/\text{min}$. The measured temperature ranges were 20 to 900 $^{\circ}\text{C}$.

5 Scanning Electron Microscopy (SEM)

The morphology of polyurethane was studied by SEM. In the SEM, a fine beam of electrons is scanned across the specimen surface and an appropriate detector was used to collect the electrons emitted from each point. The amplified current from the detector is then displayed on a cathode-ray tube, which is scanned synchronously with the electron probe. In this way the image

is built up, line by line. In this work, JSM 35 CF was used to examine compatibility between PU and PU/PS elastomer.



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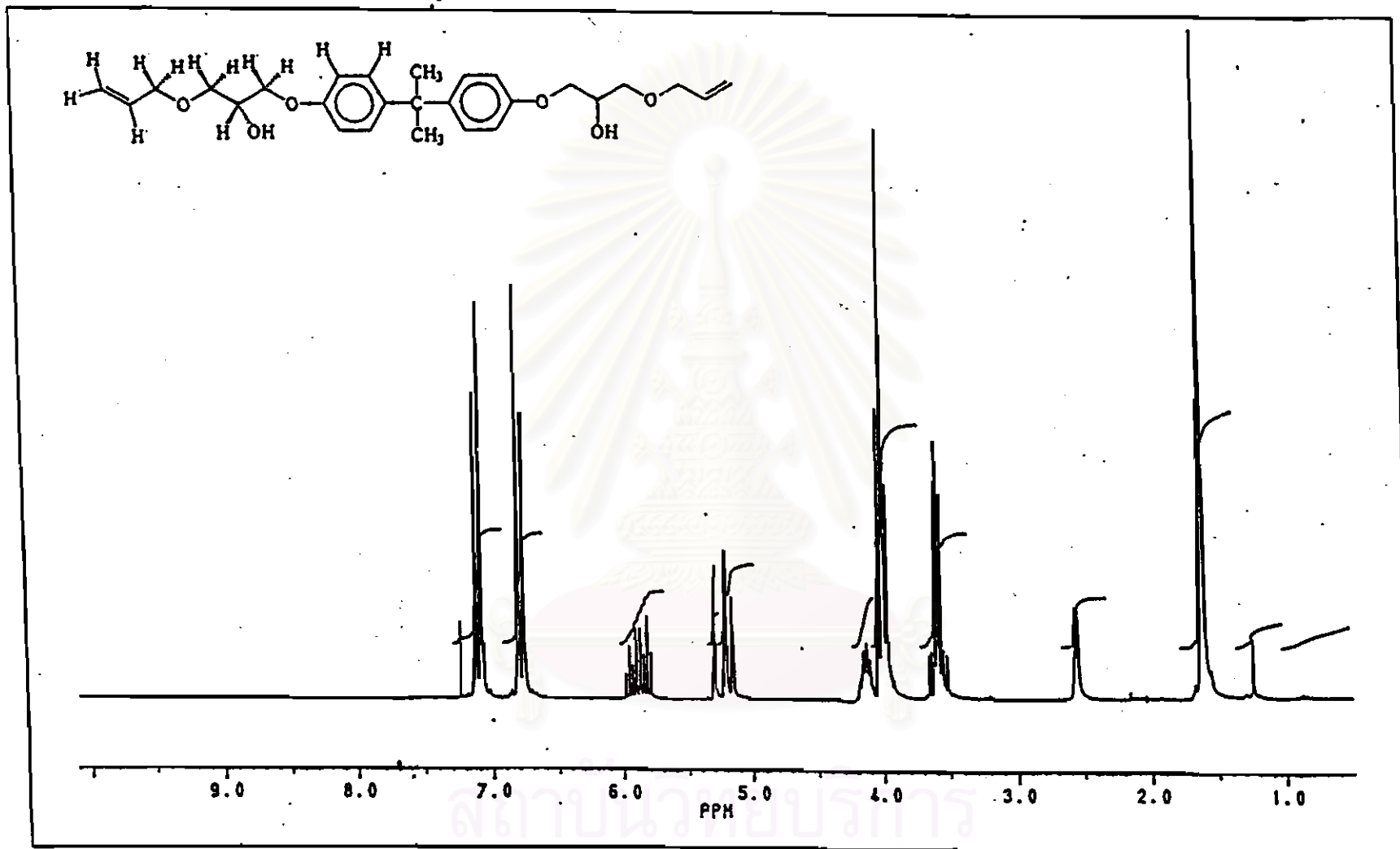


Figure A1 ¹H-NMR spectrum (CDCl₃) of Bis-(3-allyloxy-2-propanol) diphenylpropane (BAPD)

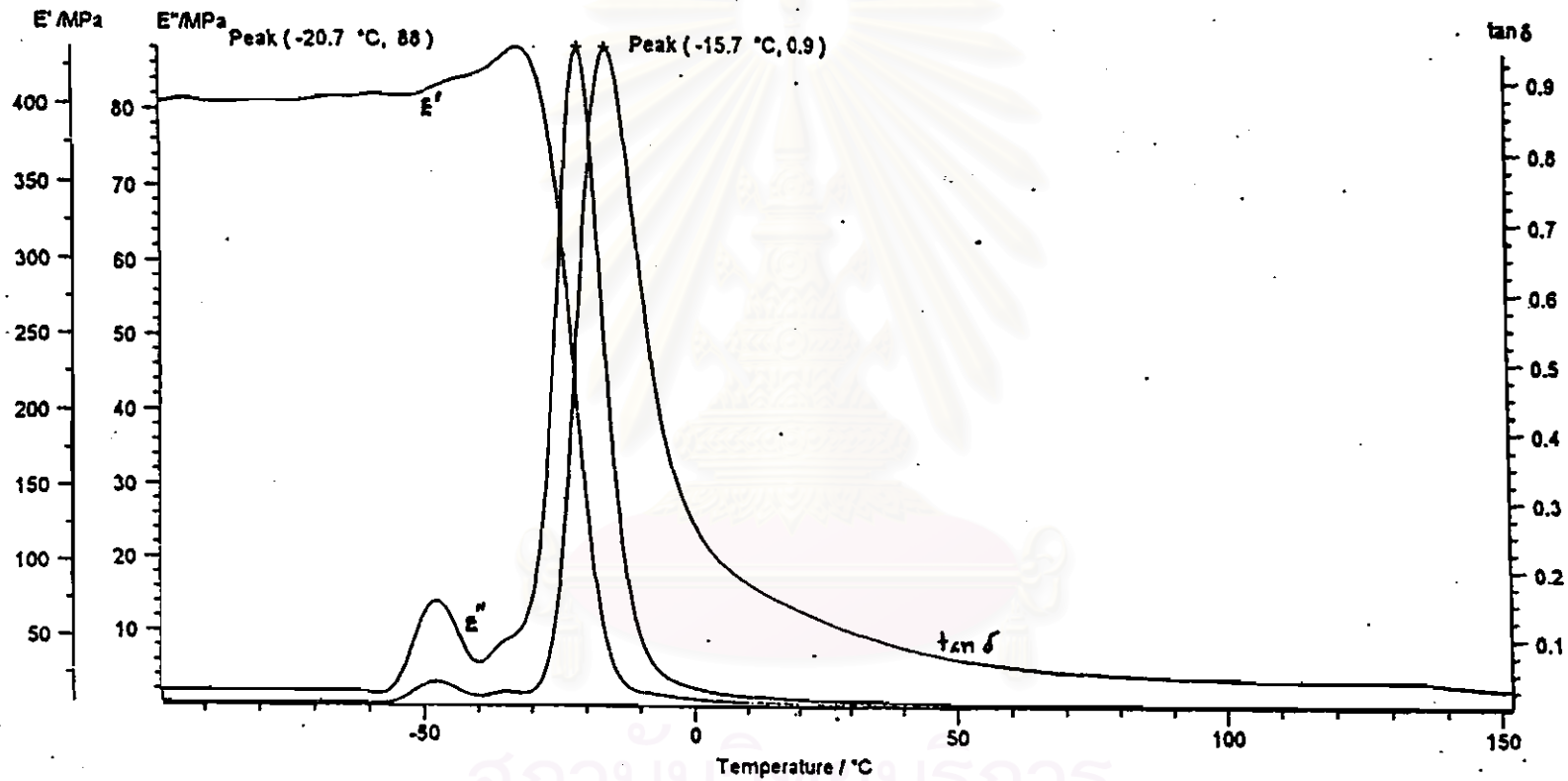


Figure A2 DMA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 10 wt% of styrene monomer, and 2 wt% of MEKP-Co.

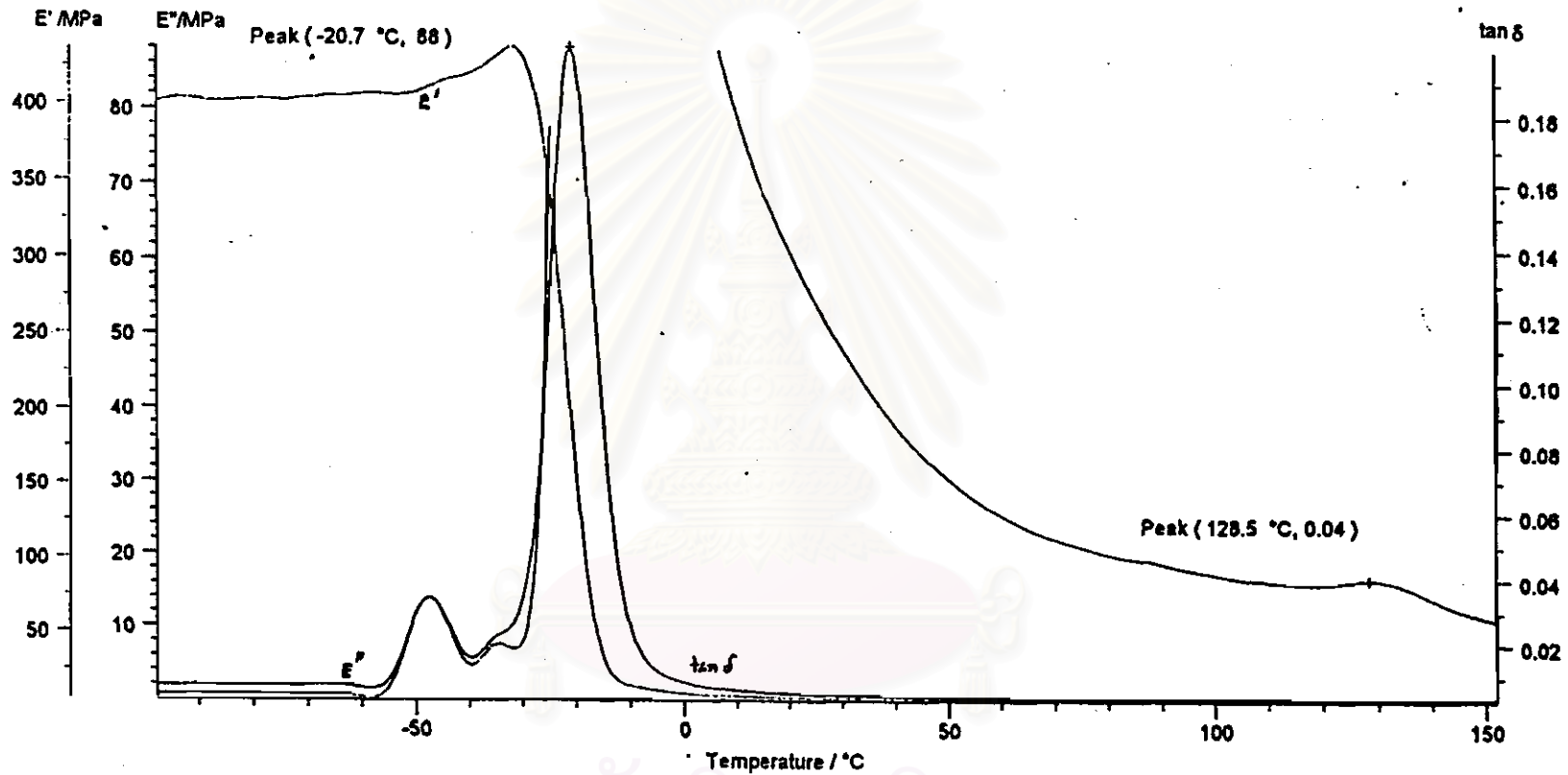


Figure A3 DMA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 10 wt% of styrene monomer, and 2 wt% of MEKP-Co.

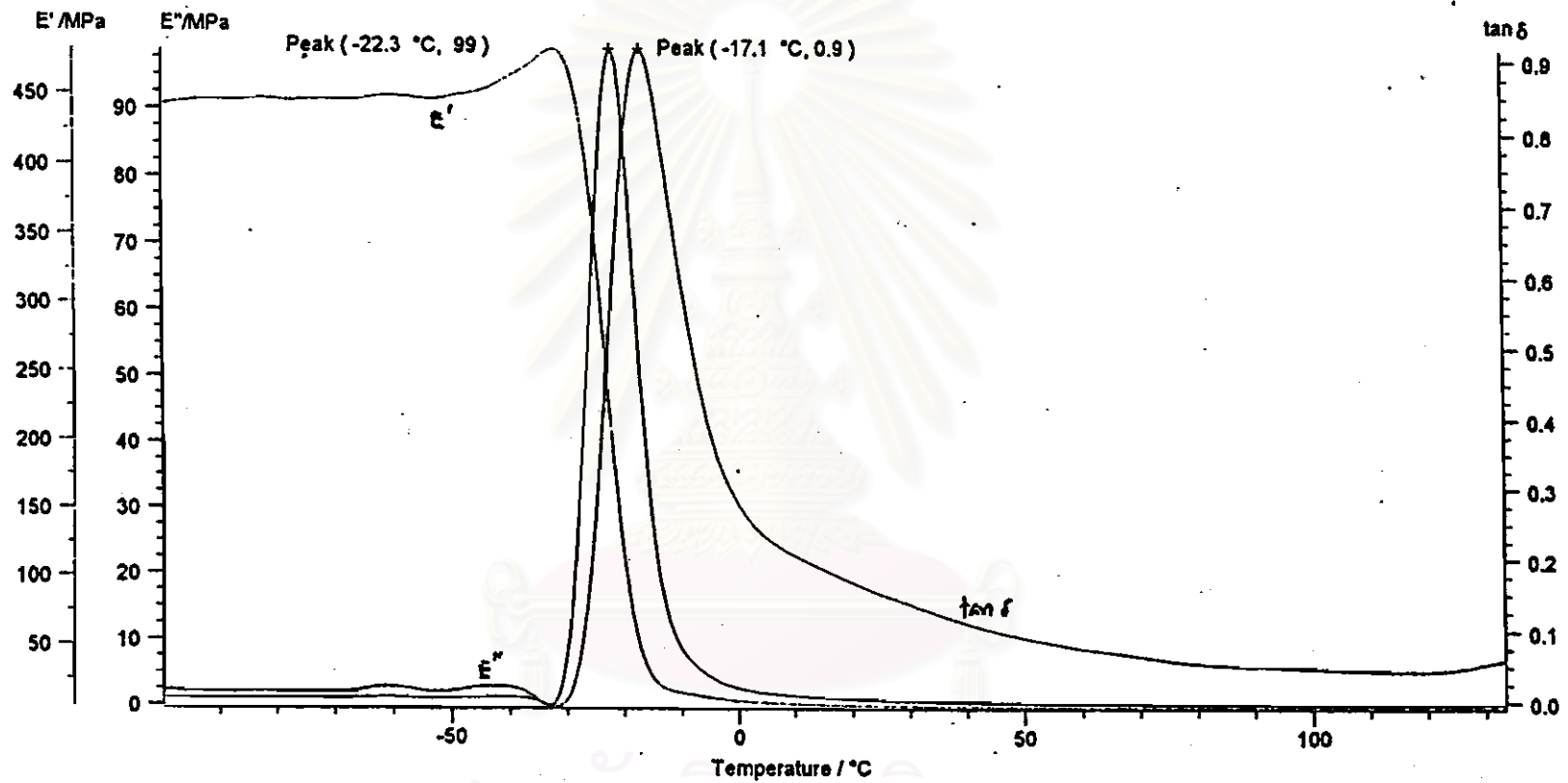


Figure A4 DMA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 15 wt% of styrene monomer, and 2 wt% of MEKP-Co.

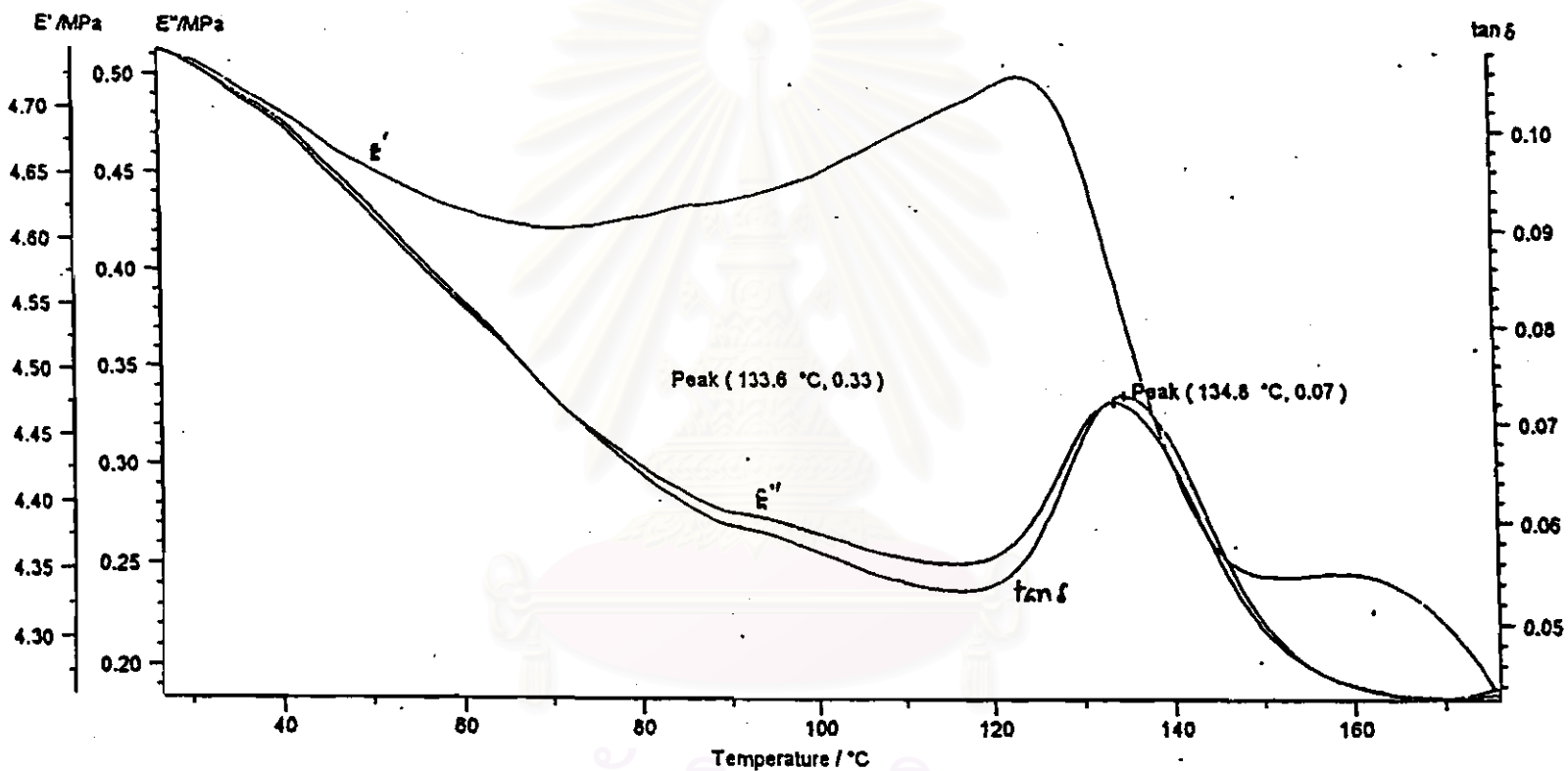


Figure A5 DMA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 15 wt% of styrene monomer, and 2 wt% of MEKP-Co.

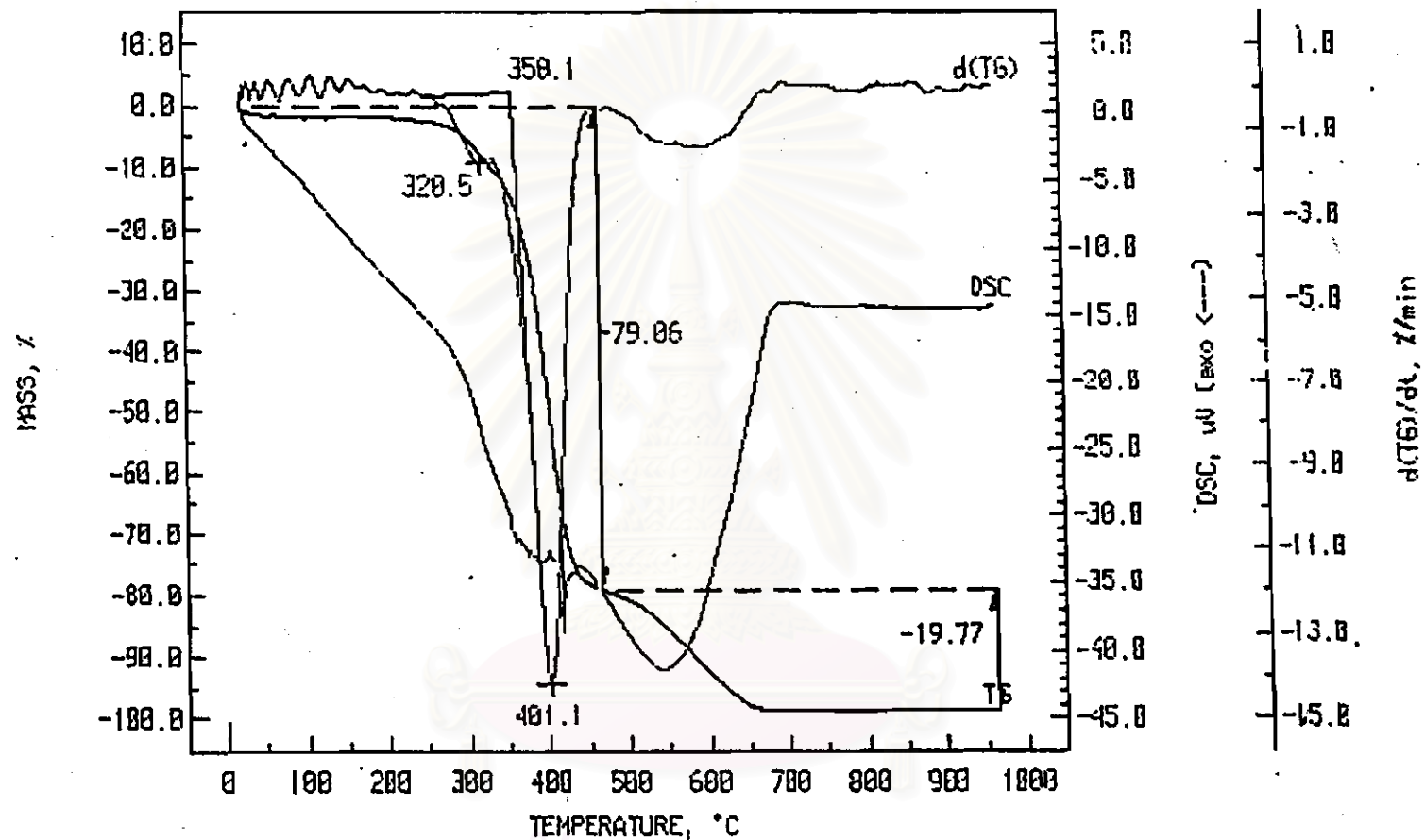


Figure A6 TGA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 10 wt% of styrene monomer, and 2 wt% of MEKP-Co.

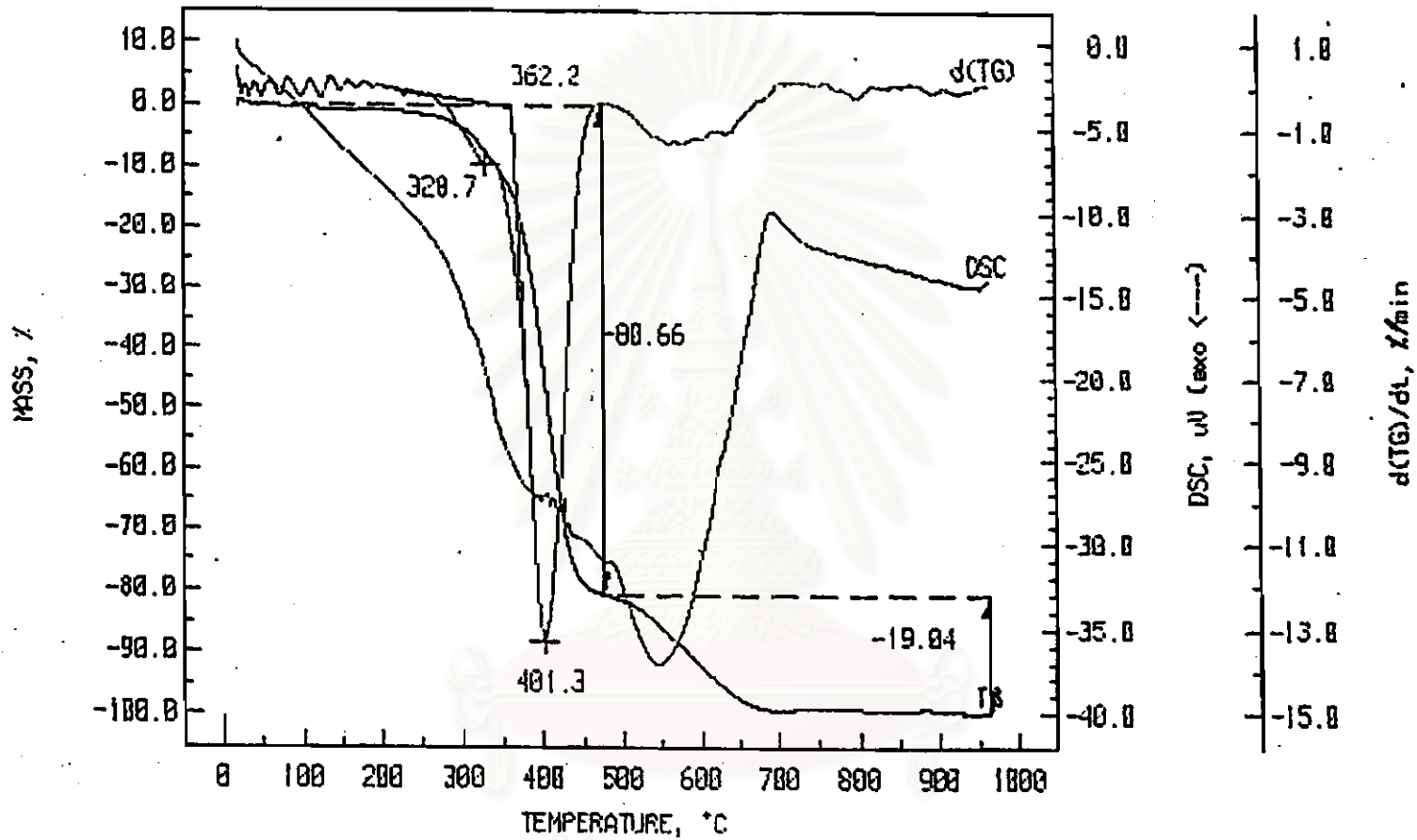


Figure A7 TGA thermogram of PU/PS elastomer at the equivalent weight ratio of MDI:Polyol:BAPD = 2:1.8:0.2, 15 wt% of styrene monomer, and 2 wt% of MEKP-Co.

VITA

Kantima Kawnaramit was born on October 13, 1972 in Samutsongkram, Thailand. She received Bachelor Degree of Science in Chemistry, Chulalongkorn University, in 1994. In the same year, she was a student in graduate school at Chulalongkorn University studying in Petrochemistry and Polymer Science and has been studying since then. She graduated with Master Degree of Science in 1997.



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