CHAPTER IV

RESULTS

4.1 The stabilizing effect of Triton X-100

In order to prevent coagulation of latex during enzyme treatment and enhance nitrogen reduction, the nonionic detergent, Triton X-100 was added as a stabilizer. By varying the concentration of Triton X-100 from 0.4-1.2 p.h.r., Table 4.1 shows that 1.1 p.h.r. is the suitable concentration to prolong latex coagulation during the papain treatment, but allows coagulation after autoclaving at 121 ^{o}C under pressure 15 lb/in^2 for 10 minutes and results in maximum nitrogen reduction about 81 %. Concentration of Triton X-100 in the range of 0.4 - 1.0 p.h.r. is too low to stabilize the latex during enzyme treatment, and the concentration higher than 1.1 p.h.r. prevents coagulation well even under steam pressure.

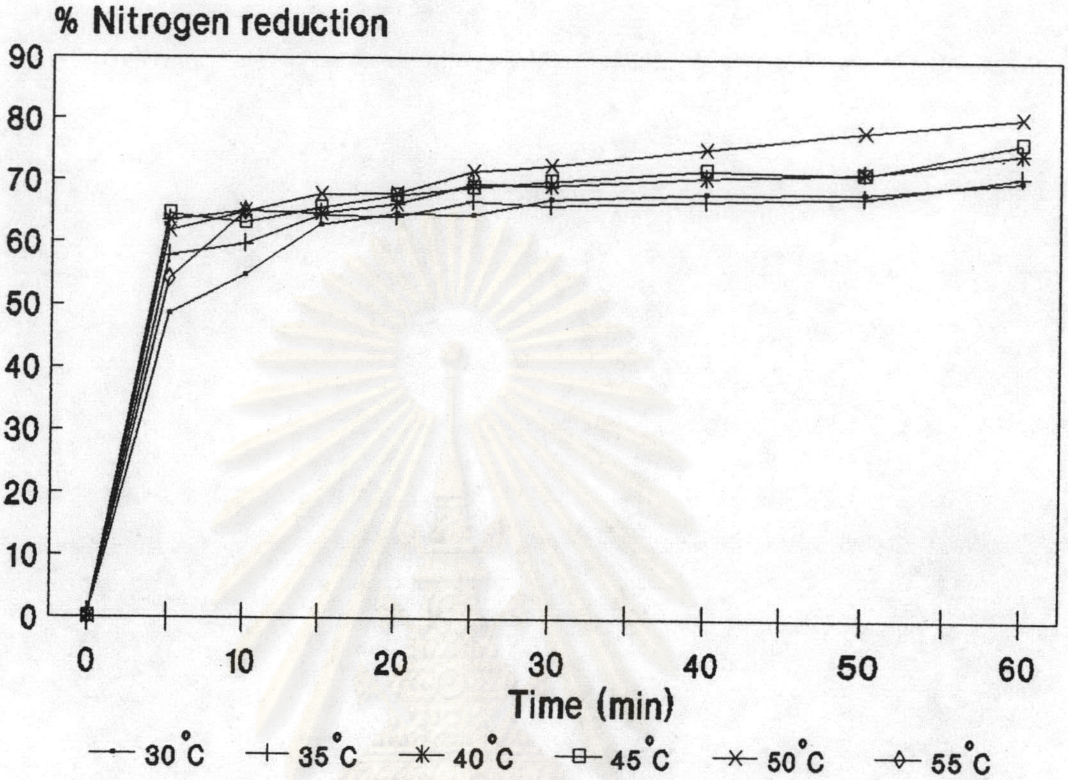
Table 4.1 The stabilizing effect of Triton X-100 at various concentrations. Deproteinization of latex (25 %DRC) was conducted in a 41 cm diameter reactor at 0.3 p.h.r. papain concentration, pH 7.6 and at agitation speed 37 rpm, 50 °C for 1 hour.

Triton X-100 (p.h.r.)	Clotting during papain treatment	Clotting after steam treatment	% Nitrogen reduction
0.0	Yes	Yes	69.13
0.4	Yes	Yes	74.28
0.9	Yes	Yes	76.27
1.0	Yes	Yes	78.30
1.1	No	Yes	80.80
1.2	No	No	ND*

Note : ND*, % N reduction was not determined, because the latex was not coagulated.

4.2 Effect of temperature on deproteinization

By varying temperature of enzyme treatment in the range of 30-50 °C, Figure 4.1 shows that papain is most effective at 50 °C as evident by the reduction of per cent nitrogen content with time and temperature. At 55 °C, the latex is not stable and coagulation occurred resulting in a decrease in per cent nitrogen reduction lower than at 50 °C. This suitable temperature of 50 °C is therefore chosen



Latex (RRIM 600) was adjusted to 25 % DRC, pH 7.6 and treated with Triton X-100 1.1 p.h.r. and papain 0.3 p.h.r. in a reactor (41 cm diameter) at agitation speed of 37 rpm at varying temperature 30, 35, 40, 45, 50 and 55 °C

Figure 4.1 Effect of temperature on deproteinization for papain treatment in the next experiments because nitrogen content is reduced to 0.11 % (about 81 % nitrogen reduction) within only one hour.

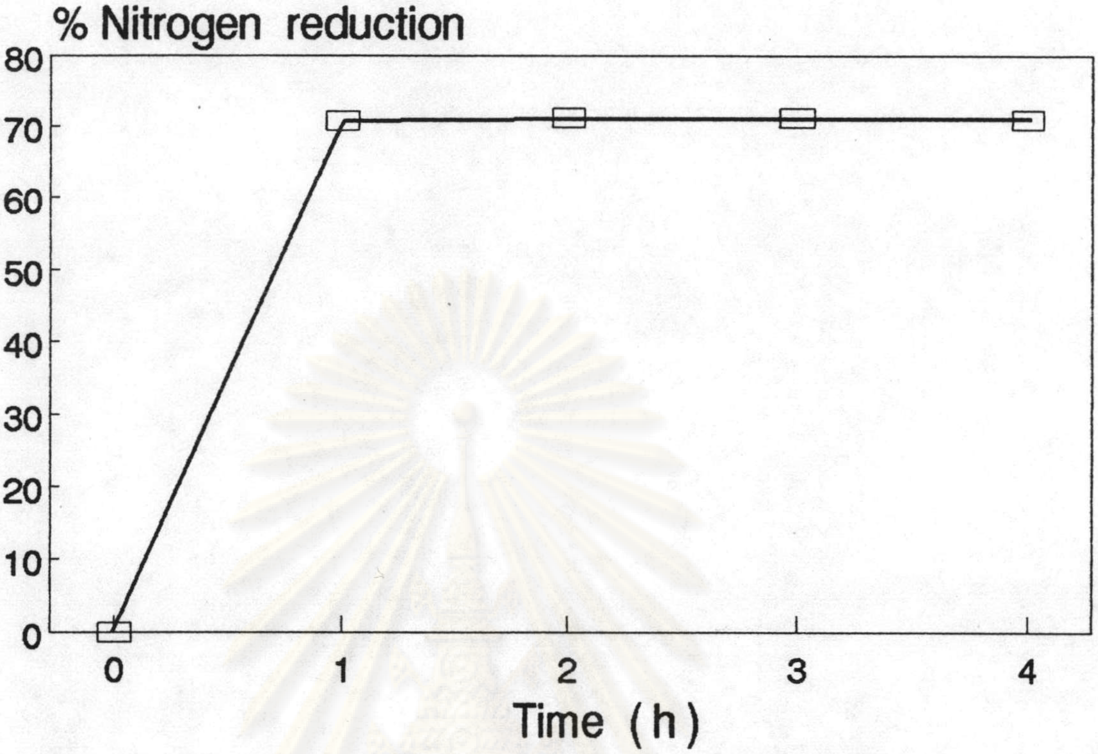
4.3 Effect of agitation speed on deproteinization

To study the effect of agitation on deproteinization, two reactors of different size were used. The first reactor was a stir-tank of 11 cm inside diameter with a constant speed 8.9 cm impeller at 57 rpm. The second reactor was a vessel of 41 cm inside diameter with a 28 cm impeller. The agitation speed of this impeller can be adjusted in the range of 37-200 rpm.

Maximum deproteinization in the 11 cm diameter reactor at 57 rpm fixed-speed (Re = 120) can be obtained after 1 hour or longer digestion at 50 ^{o}C, resulted in about 71 % nitrogen reduction (Figure 4.2). The remaining nitrogen content was 0.16 %, which is still higher than DPNR specification (N < 0.12 %).

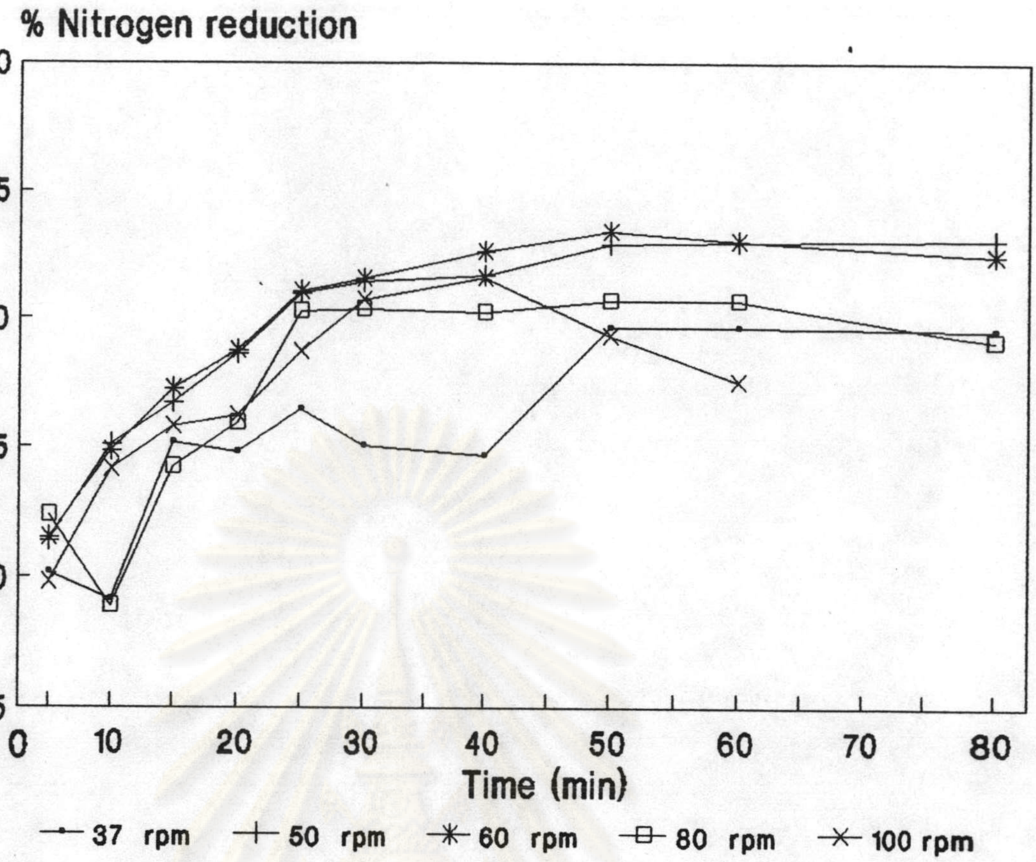
Deproteinization by using the 41 cm diameter reactor at agitation speed ranging from 37-100 rpm (770 < Re < 2100) resulted in various nitrogen reduction from 78-84 % after 1 hour of papain treatment at 50 ^{o}C as shown in Figure 4.3. The highest reduction of nitrogen (84 %) was obtained at the agitation speed of 60 rpm, 50 minutes and the final nitrogen content of 0.096-0.104 % which are lower than DPNR specification can also be obtained under this condition.

At agitation speed of 37 rpm and 50 rpm, the per cent nitrogen reduction fluctuated between 75-80 % (0.12-0.14 % nitrogen content) and 80-83 % (0.10-0.12 % nitrogen content) respectively. At agitation



Latex (RRIM 600) was adjusted to 25 % DRC, pH 7.6 and treated with Triton X-100 1.1 p.h.r. and papain 0.3 p.h.r. at temperature 50 ^{o}C at agitation speed 57 rpm

Figure 4.2 Effect of time on deproteinization using a reactor of 11 cm diameter at 57 rpm impeller speed



Latex (RRIM 600) was adjusted to 25 % DRC, pH 7.6 and treated with Triton X-100 1.1 p.h.r. and papain 0.3 p.h.r. in a reactor at temperature 50 ^{o}C at varing agitation speed 37, 50, 60, 80 and 100 rpm

Figure 4.3 Effect of various agitation speed on deproteinization using a reactor of 41 cm diameter speed over 60 rpm, the latex was unstable and coagulation occurred resulting in the decrease of per cent nitrogen reduction lower than 80 %.

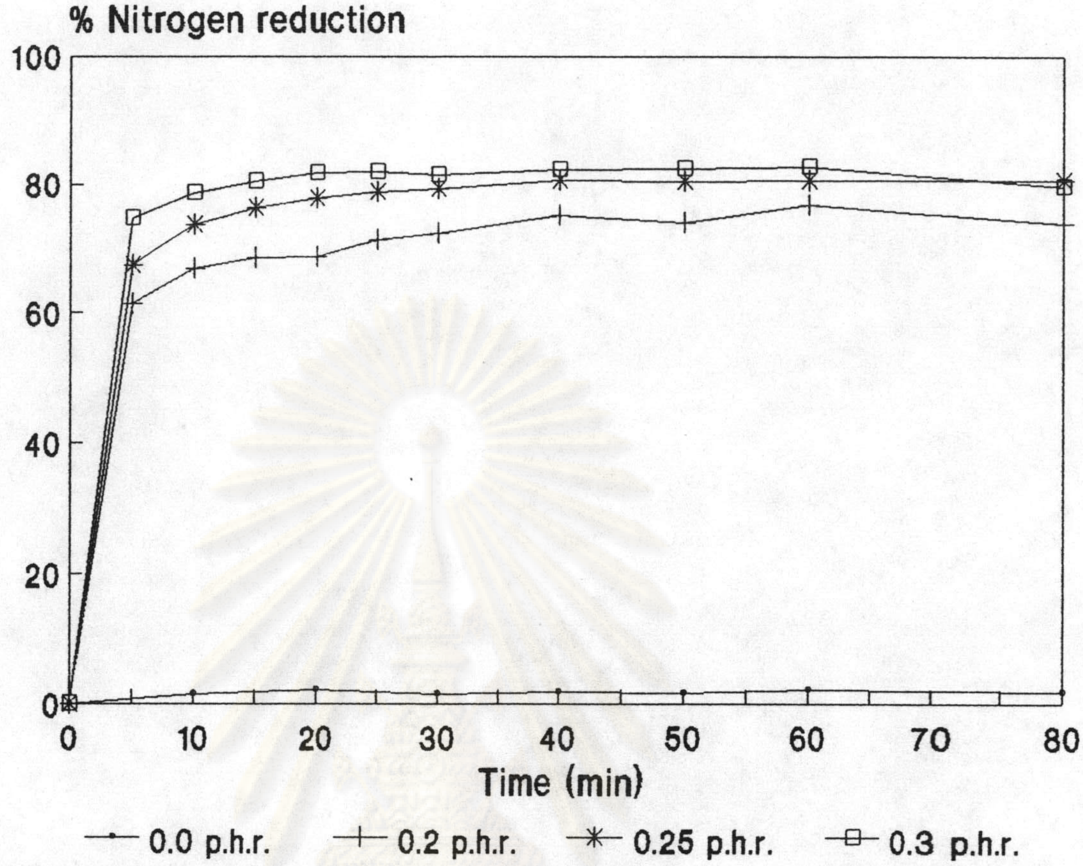
4.4 Effect of papain concentration on deproteinization

To be assured that the concentration of papain is suitable for deproteinization, fresh latex was added with various papain concentration ranging from 0 to 0.3 p.h.r.. Figure 4.4. shows that the per cent nitrogen reduction is dependent on papain concentration. At the suitable concentration of 0.3 p.h.r., nitrogen content can be reduced to 0.10 %, whereas at lower papain concentration of 0.2 and 0.25 p.h.r., the final nitrogen content were higher than DPNR specification (0.12 %).

4.5 Effect of deproteinization on the molecular weight distribution

Since weight average molecular weight (Mw) and molecular weight distribution (MWD) of natural rubber are important criteria of rubber quality, it is necessary to make sure that there is no degradation of the rubber molecules under the conditions used for deproteinization. Figure 4.5 a-e shows the comparative study of MWD between the CV-DPNR with the control non-deproteinized rubber prepared from 4 rubber clones ; RRIM 600, PB 28/59, PB 5/51 and GT 1 and commercial rubber grades ; TTR 5L, white crepe rubber and RSS 1.

The MWD of solid dry rubber obtained from Hevea latex shows a bimodal ditribution of 2 peaks. All rubber clones show the high molecular weight peak ranges from about 1.3-1.8 x 10^6 with shoulder of the low molecular weight ranging from about 10^4-10^5, where the



Latex (RRIM 600) was adjusted to 25 % DRC, pH 7.6 and treated with Triton X-100 1.1 p.h.r. in a reactor (41 cm diameter) at agitation speed of 60 rpm at varying papain concentration 0, 0.20, 0.25 and 0.3 p.h.r.

Figure 4.4 Effect of papain concentration on deproteinization

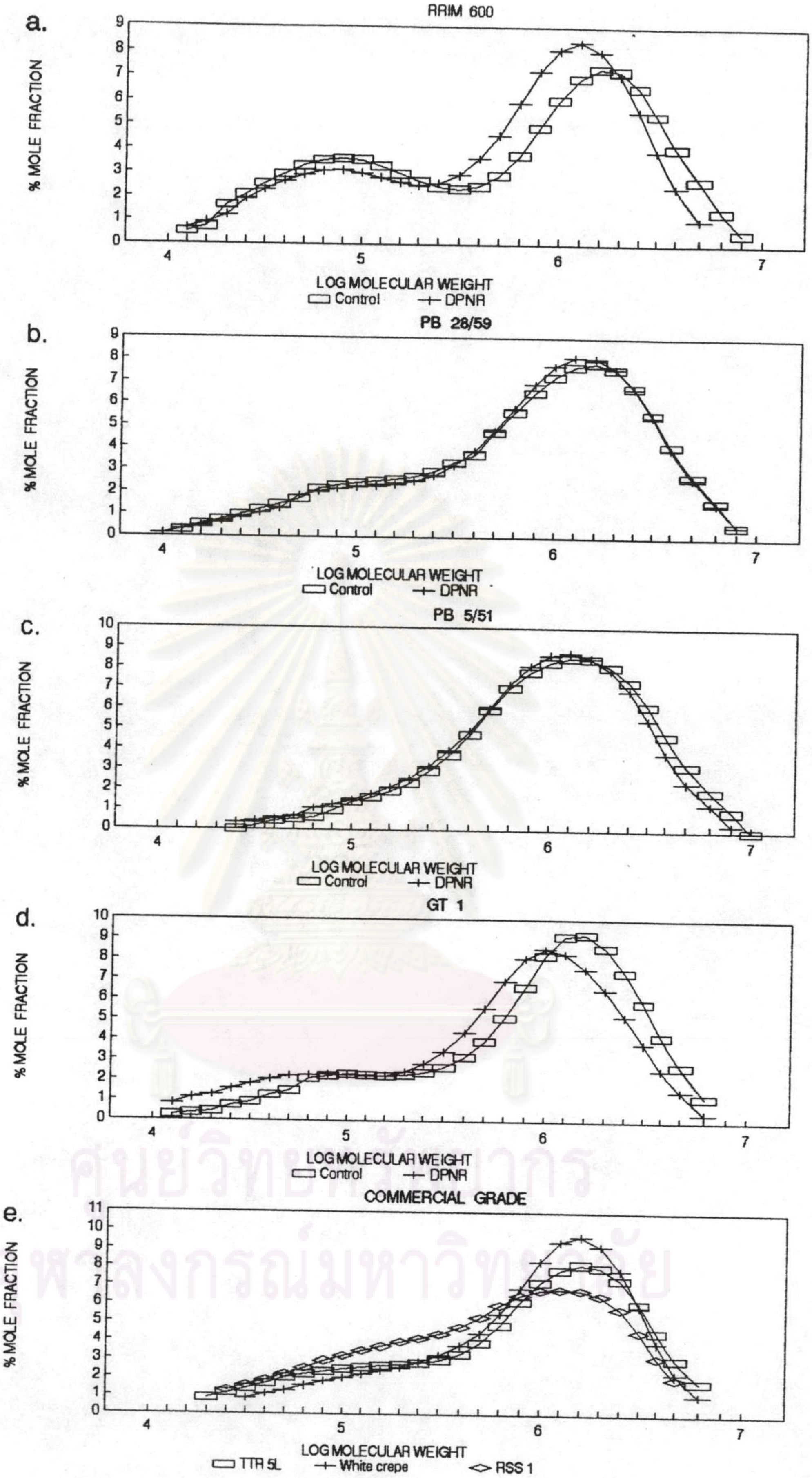


Figure 4.5 The comparative study of MWD between the CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades ; a. RRIM 600, b. PB 28/59, c. PB 5/51 d. GT 1 and e. commercial rubber grades

total molecular weight or MWD covers the range of 10^4 and 10^7. The weight average molecular weight (Mw) of 1.1-1.7 x 10^6 and the number average molecular weight (Mn) of 1.5-5.7 x10^5 were observed depending on the clonal characteristics (Table 4.2). PB 5/51 showed the highest Mw and Mn followed by GT 1, PB 28/59 and RRIM 600 respectively. The molecular weight distribution characteristics of rubber can be expressed by polydispersity (Mw/Mn). RRIM 600, PB 28/59 and GT 1 have high polydispersity (5-9) and bimodal distribution, but PB 5/51 has distinguished lower polydispersity around 3 and unimodal distribution.

Deproteinization has no drastic effect on the molecular weight distribution of all 4 rubber clones as compared to their non-deproteinized control rubbers and the other specimens of commercial grades rubber ; TTR 5L and white crepe. It is noted that RSS 1 shows higher proportion of the small Mw fraction.

Table 4.2 Weight average molecular weight (Mw), number average molecular weight (Mn) and molecular weight distribution (MWD) or polydispersity of CV-DPNR, its control and commercial rubber grades.

	RRIM 600		PB 28/59		PB 5/51		GT 1		TTR 5L	White crepe	RSS 1
	Control CV–NR	CV–DPNR	Control CV–NR	CV–DPNR	Control CV–NR	CV–DPNR	Control CV–NR	CV–DPNR			
Mn x 10^{-5} (from GPC)	1.52	2.06	2.76	2.92	5.65	5.55	3.70	2.34	2.46	3.78	2.29
Mw x 10^{-6} (from GPC)	1.36	1.37	1.47	1.48	1.69	1.65	1.53	1.44	1.51	1.50	1.15
Mw x 10^{-6} at peak maximun	1.78	1.39	1.59	1.56	1.42	1.46	1.67	1.42	1.67	1.67	1.33
Polydispersity	9.06	6.80	6.22	6.11	3.15	3.16	5.28	6.28	6.15	3.98	5.02

4.6 Properties of CV-DPNR

4.6.1 Physical properties of raw rubber

The physical properties that determine the quality of raw rubber are compared between CV-DPNR and its control CV-NR of the same clone and the commercial rubber grades; TTR 5L, white crepe and ribbed smoked sheet 1 (RSS 1). Figure 4.6a shows the significant reduction in nitrogen content from 0.383-0.587 to 0.036-0.094 or 81.53-90.60 % depending on the rubber clone. The CV-DPNR produced from clones : RRIM 600, PB 28/59 and PB 5/51 have their nitrogen content reduced by 90 %, but GT 1 has the lowest nitrogen reduction of 81 %. However the CV-DPNR of all 4 clones contain total nitrogen content lower than DPNR specification (% N < 0.12 %).

Apart from the decrease in nitrogen content, the dirt content and volatile matter are obviously decreased lower than the RRIM specification of 0.015 % and 0.5 % respectively. Only the ash contents which are higher than 0.15 % limit (Figure 4.6b-d). Deproteinization improves rubber color, as evident by the color index of all CV-DPNR is lower than 4. The deproteinized rubber obtained from clone RRIM 600 and PB 5/51 have lower color index than PB 28/59 and GT 1 (Figure 4.6e) and lighter color (Figure 4.7).

Comparing between CV-DPNR and commercial grades rubber, most of the physical properties namely nitrogen content, dirt content, volatile matter and color index are much better than commercial grades rubber, except for the color index of GT 1 which contains high nitrogen content after enzyme treatment, that the color is not different from the light color grade commercial rubber such as TTR 5L and white crepe rubber, but still significantly better than RSS 1.

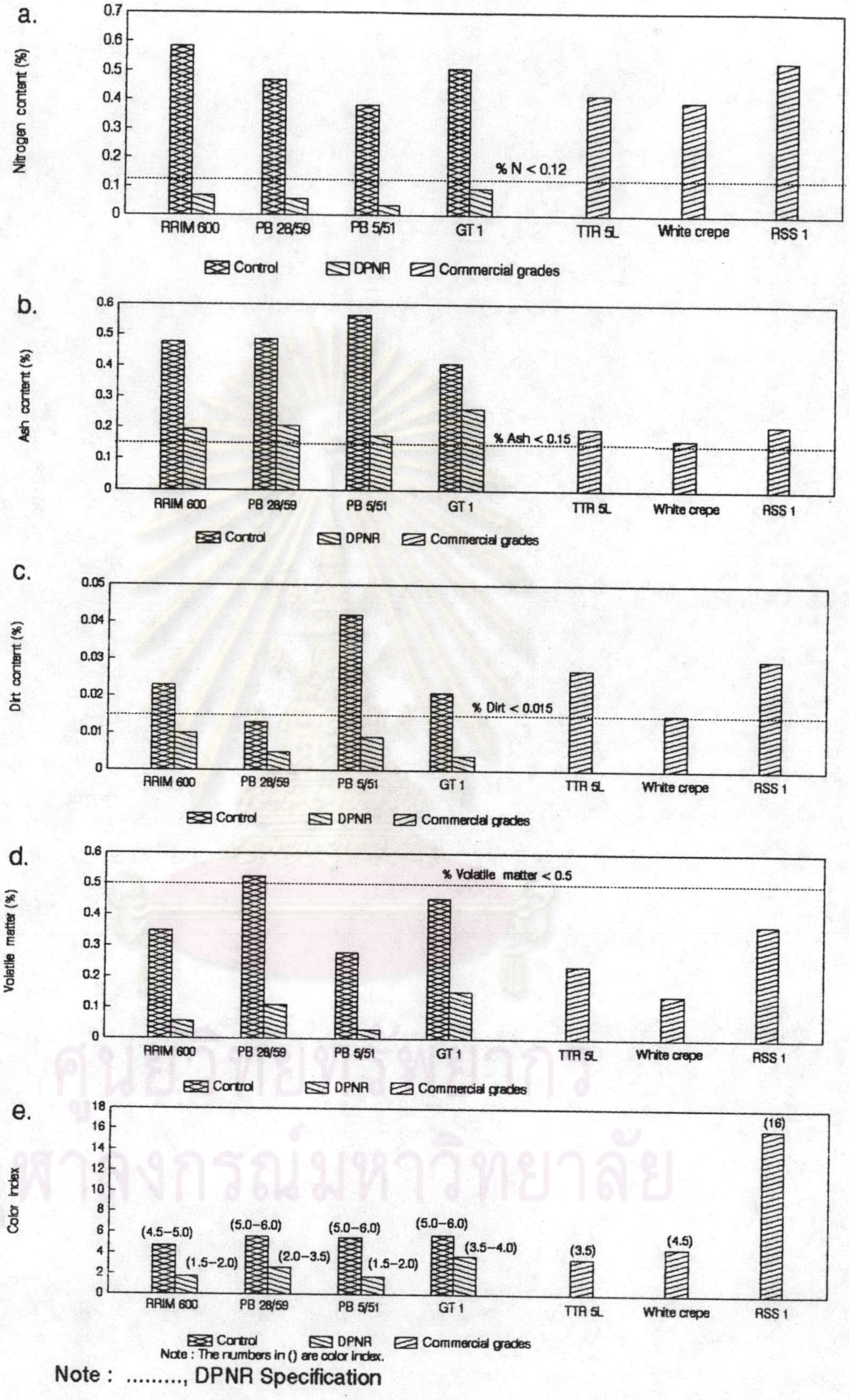


Figure 4.6 Comparison of raw rubber properties between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades. a. % nitrogen content, b. ash content, c. dirt content, d. volatile matter and e. color index

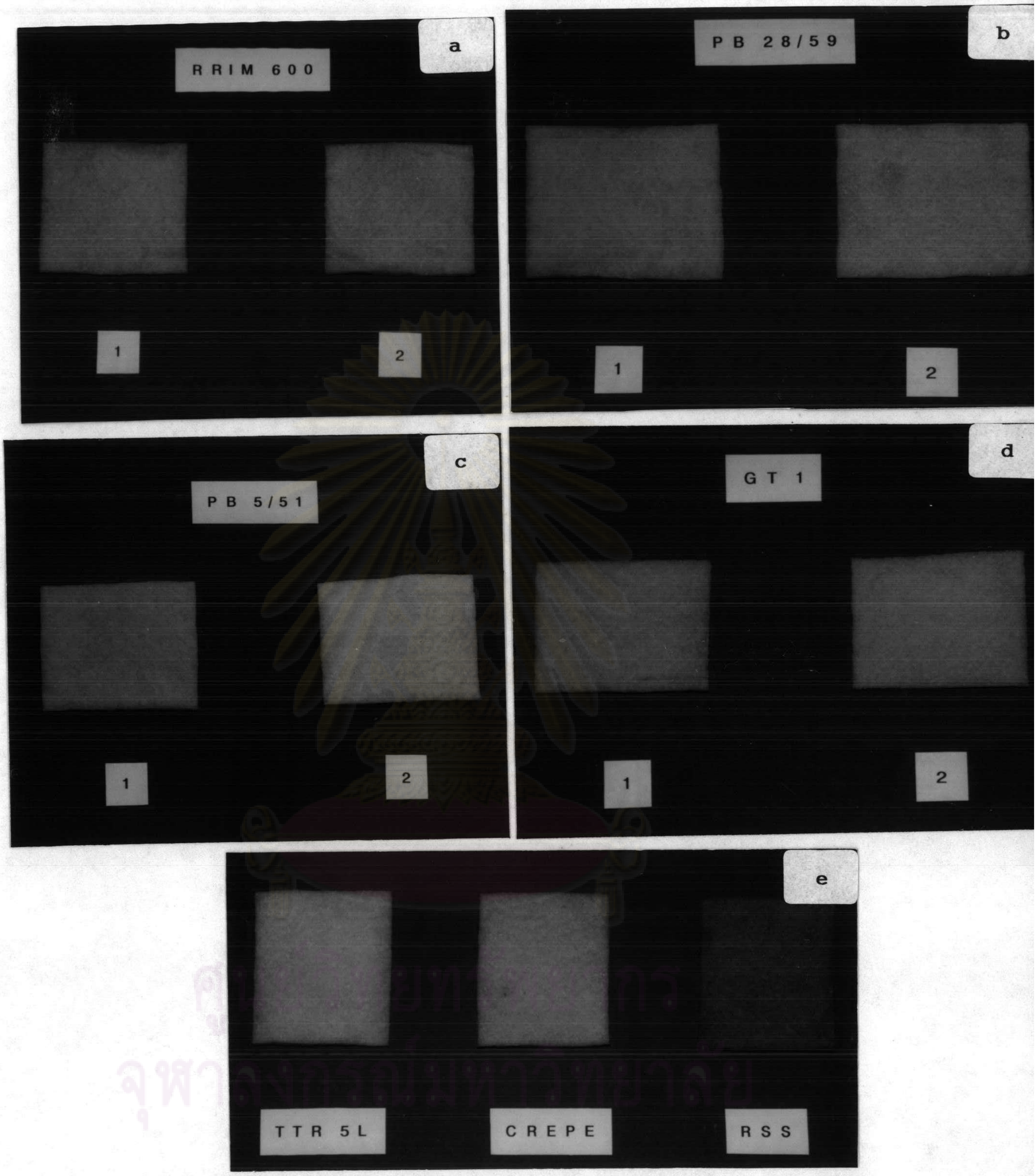


Figure 4.7 Comparison of raw rubber color between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades.

a. RRIM 600 ; b. PB 28/59 ; c. PB 5/51 ; d. GT 1 and

e. TTR 51, white crepe and ribbed smoked sheet 1 (RSS 1)

1 Control, 2 CV-DPNR

As for the Mooney viscosity and other resilient properties namely the initial plasticity (P_o), plasticity retention index (PRI) and storage hardening, Figure 4.8 shows a slight decrease of P_o and Mooney viscosity in CV-DPNR comparing to its control sample about 3-5 unit and 1-3 unit respectively. The PRI of CV-DPNR is lower than its control CV-NR about 10-16 unit, but still higher than the acceptable value of 60. When the rubber samples were kept over P_2O_5 at 60 ^oC for 24 hours for storage hardening test (ΔP), ΔP lower than 9 can be acheived in all clones of CV-NR. The increase of ΔP of control CV-samples is higher than CV-DPNR samples for about 3-6 unit, which indicates that CV-DPNR should withstand storage hardening better than CV-NR.

Comparing the resilient properties between CV-DPNR and commercial rubber grades, the CV-DPNR has outstanding quality regarding the ΔP. The Mooney viscosity of CV-DPNR of all clones is lower than commercial rubber grades except PB 5/51, as well as the PRI, although the PRI of RRIM 600 is better than white crepe.

To confirm that the Mooney viscosity of rubber samples can be stabilized during storage, the rubber samples were kept at room temperature for 7-10 months. Figure 4.9 shows that Mooney viscosity of all samples slightly increased 1-6 units except with highest increase of RSS 1 at 10 units.

4.6.2 <u>Cure characteristics</u>

CV-DPNR rubber samples, control CV-NR and commercial grade rubbers were compounded with compound additives on a two-roll mill at room temperature, left for 24 hours, and then their cure characteristics were studied using a Rheometer. Cure characteristics

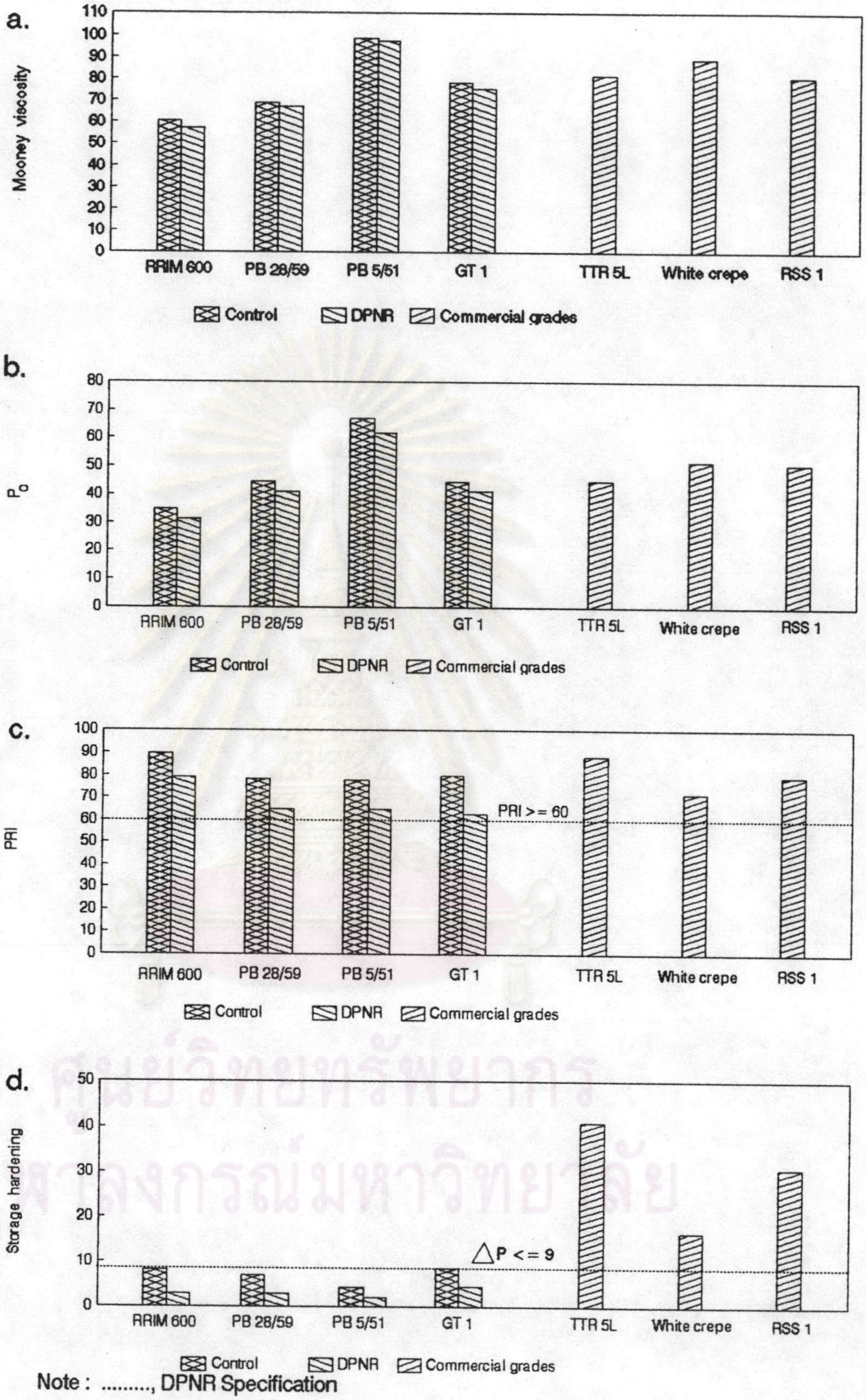


Figure 4.8 Comparison of the physical properties of raw rubber between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades.

a. Mooney viscosity, b. P_O, c. PRI and d. storage hardening

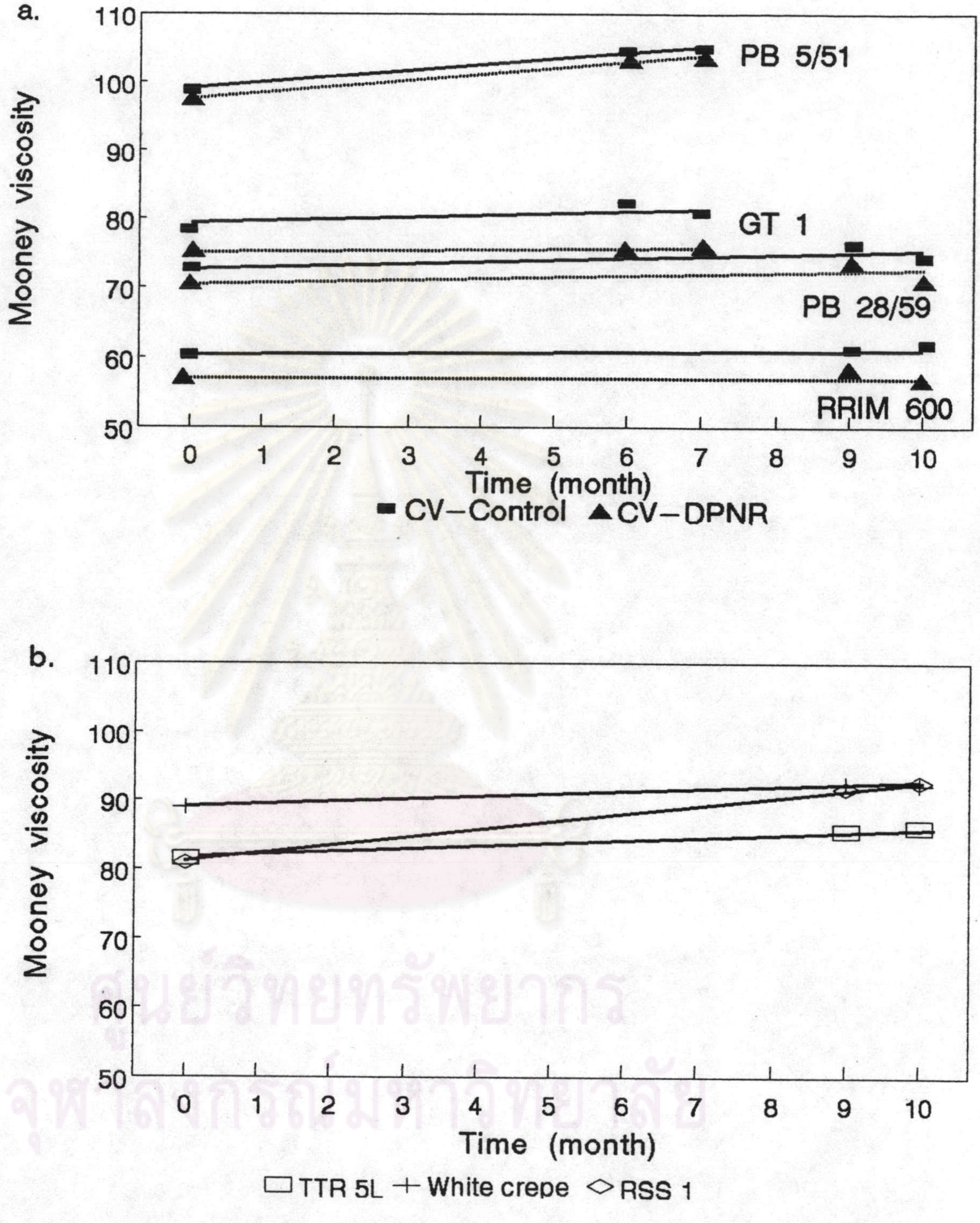


Figure 4.9 Mooney viscosity before and after storage

a. CV Rubber from 4 clones and b. commercial rubber grades such as scorch time, cure time, cure rate and torque rise are compared, as shown in Figure 4.10. All the deproteinized rubber has increased scorch time (t_s) significantly in all 4 clones from 1.48-1.87 minutes to 1.64-2.14 minutes. The cure time (t_{90}) and cure rate (t_{90}-t_s) of deproteinized rubber decreased in RRIM 600, PB 28/59 and GT 1 but increased in PB 5/51. The torque rise (M_H-M_L) of CV-DPNR decreased except for RRIM 600.

Comparison between the cure characteristics of CV-DPNR and commercial grades shows that the CV-DPNR has longer scorch time, but similar cure time as TTR 5L and white crepe. The cure rate of CV-DPNR are lower than all commercial grades; TTR 5L, white crepe and RSS 1. The torque rise of RRIM 600 and PB 28/59 are about the same of TTR 5L, but PB 5/51 and GT 1 show about half torque rise comparing to the high protein rubbers.

The color of compound rubbers were different depending on the source of rubber and the chemical ingredients added in compound formulation. The compound CV-DPNR for all rubber clones have slightly lighter color than its control and high protein commercial grades especially RSS 1 (Figure 4.11).

4.6.3 <u>Properties of vulcanizates</u>

The properties of vulcanizates, control CV-NR, CV-DPNR and commercial grade rubber samples are shown in Figure 4.12. After papain treatment an increase in tensile strength, % elongation at break and tear strength can be observed, but hardness and 300 % modulus were decreased. The specific gravity of papain treated and non-treated vulcanizates are similar. RRIM 600 has the highest tensile strength and elongation at break, but the tear strength of PB 28/59, PB 5/51 and

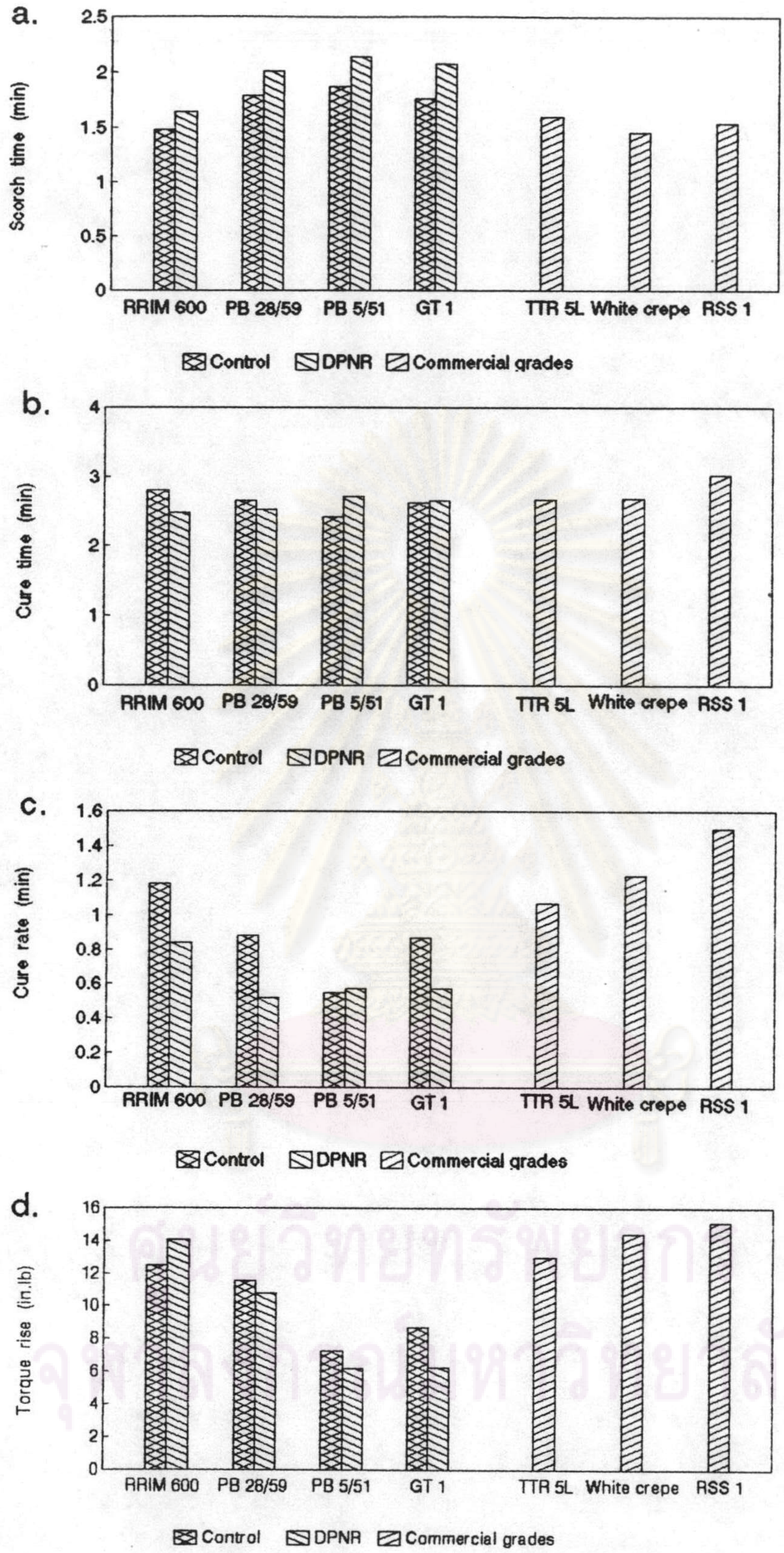


Figure 4.10 Comparison of cure characteristics between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades. a. scorch time, b. cure time, c. cure rate and d. torque rise

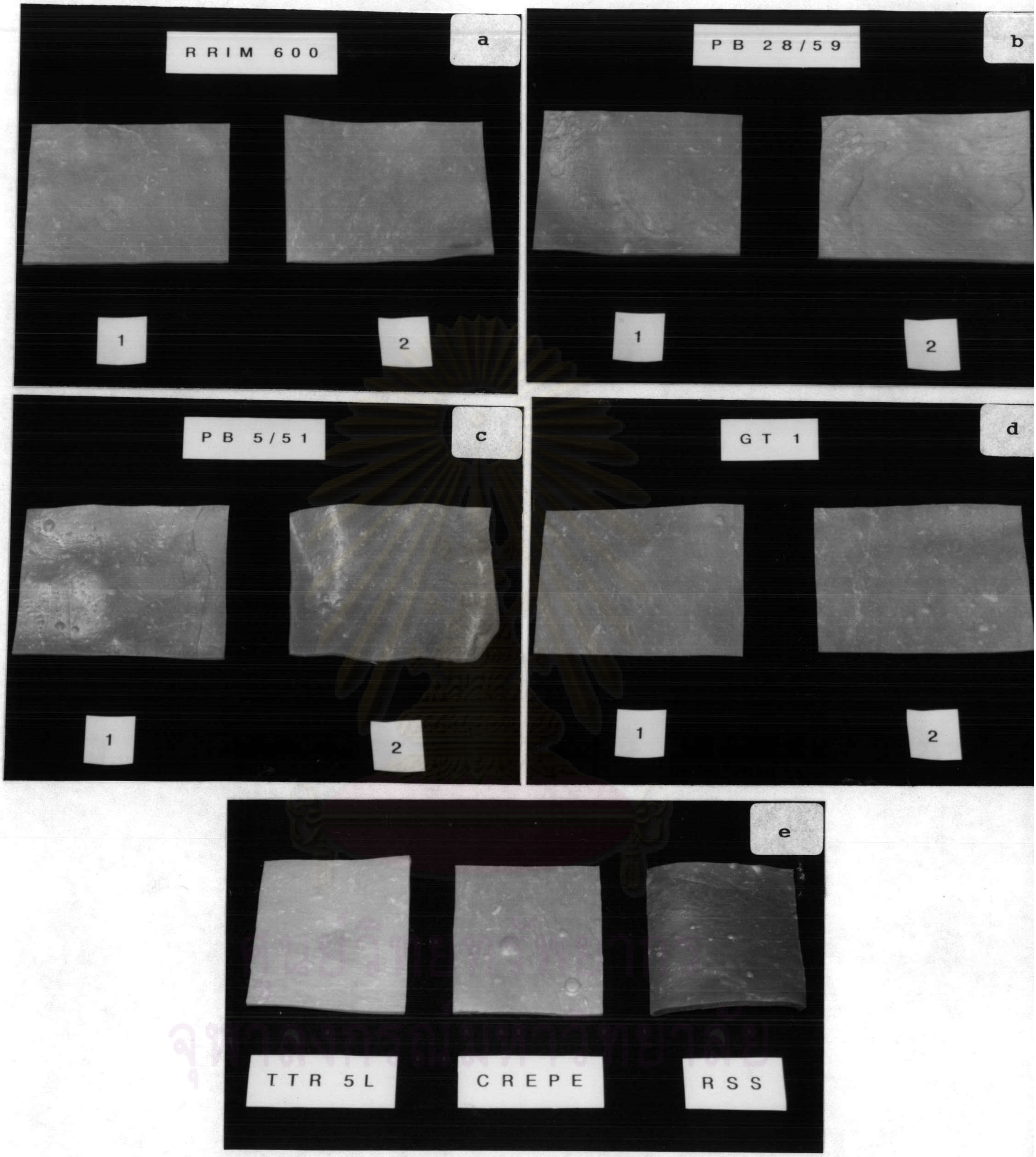


Figure 4.11 Comparison of compound rubber color between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades.

a. RRIM 600 ; b. PB 28/59 ; c. PB 5/51 ; d. GT 1 ;

e. TTR 5l, white crepe and ribbed smoked sheet 1 (RSS 1)

1 Control, 2 CV-DPNR

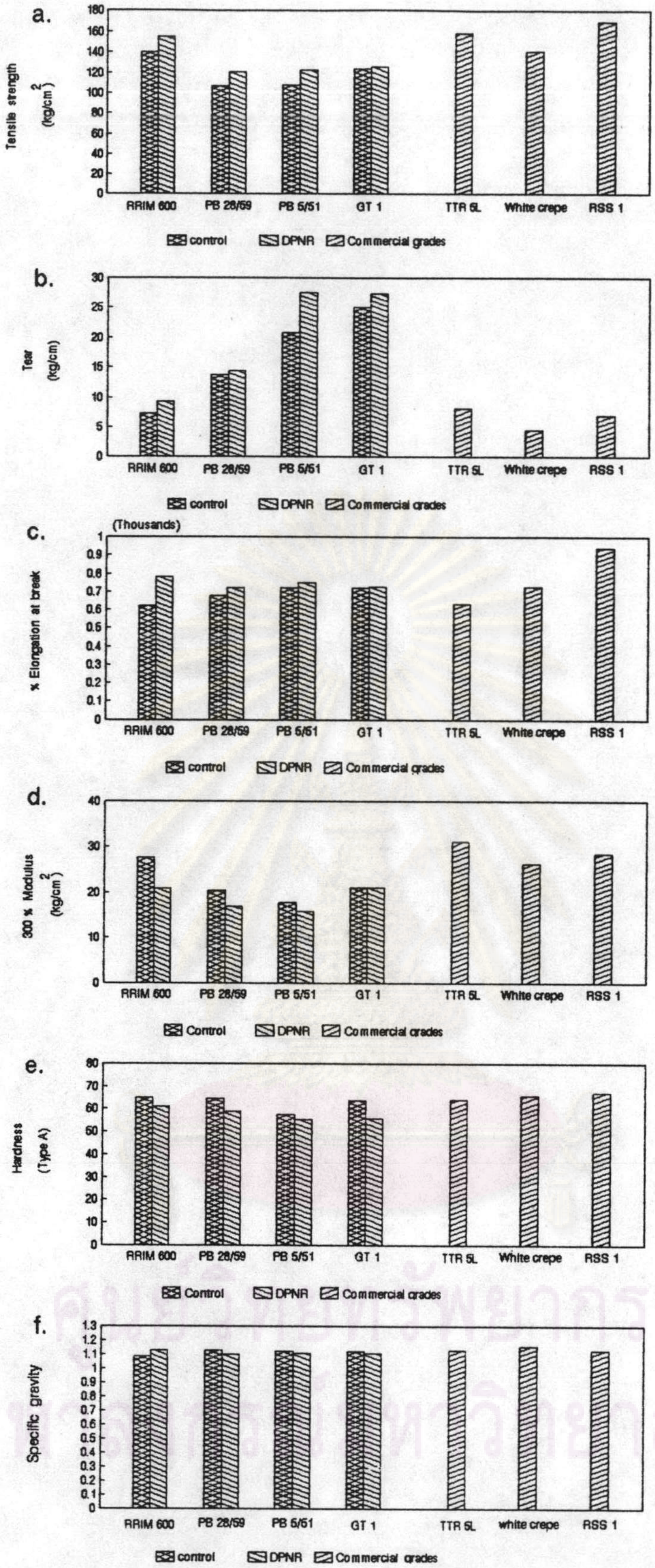
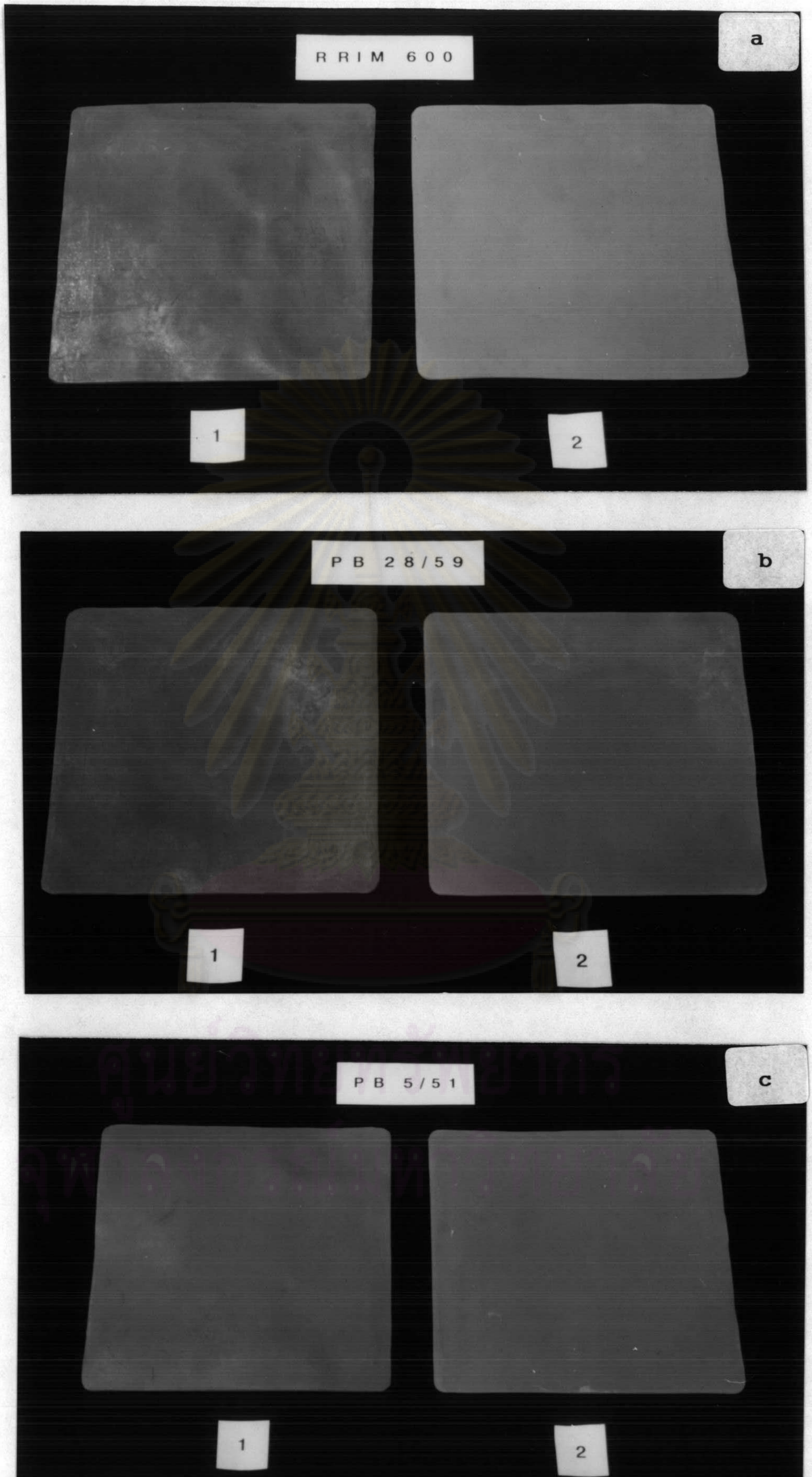


Figure 4.12 Comparison of vulcanizate properties between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades. a. tensile strength, b. tear strength, c. % elongation at break, d. 300 % modulus, e. hardness and f. specific gravity

GT 1 are higher than RRIM 600.

Comparison between CV-DPNR vulcanizates and commercial grades vulcanizates shows that the tensile strength and elongation at break are not significantly different whereas tear strength of CV-DPNR is significantly higher than commercial grade rubbers. Hardness and 300 % modulus of CV-DPNR are lower than commercial grades.

The color of CV-DPNR vulcanizates are lighter than its control and commercial grades ; TTR 5L, white crepe and RSS 1 as shown in Figure 4.13. Comparing among different clones, CV-DPNR vulcanizate from clone RRIM 600, PB 5/51 and PB 28/59 have lighter color than GT 1.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1
2
b
P B 2 8 / 5 9
1
2
c
P B 5 / 5 1
1
2

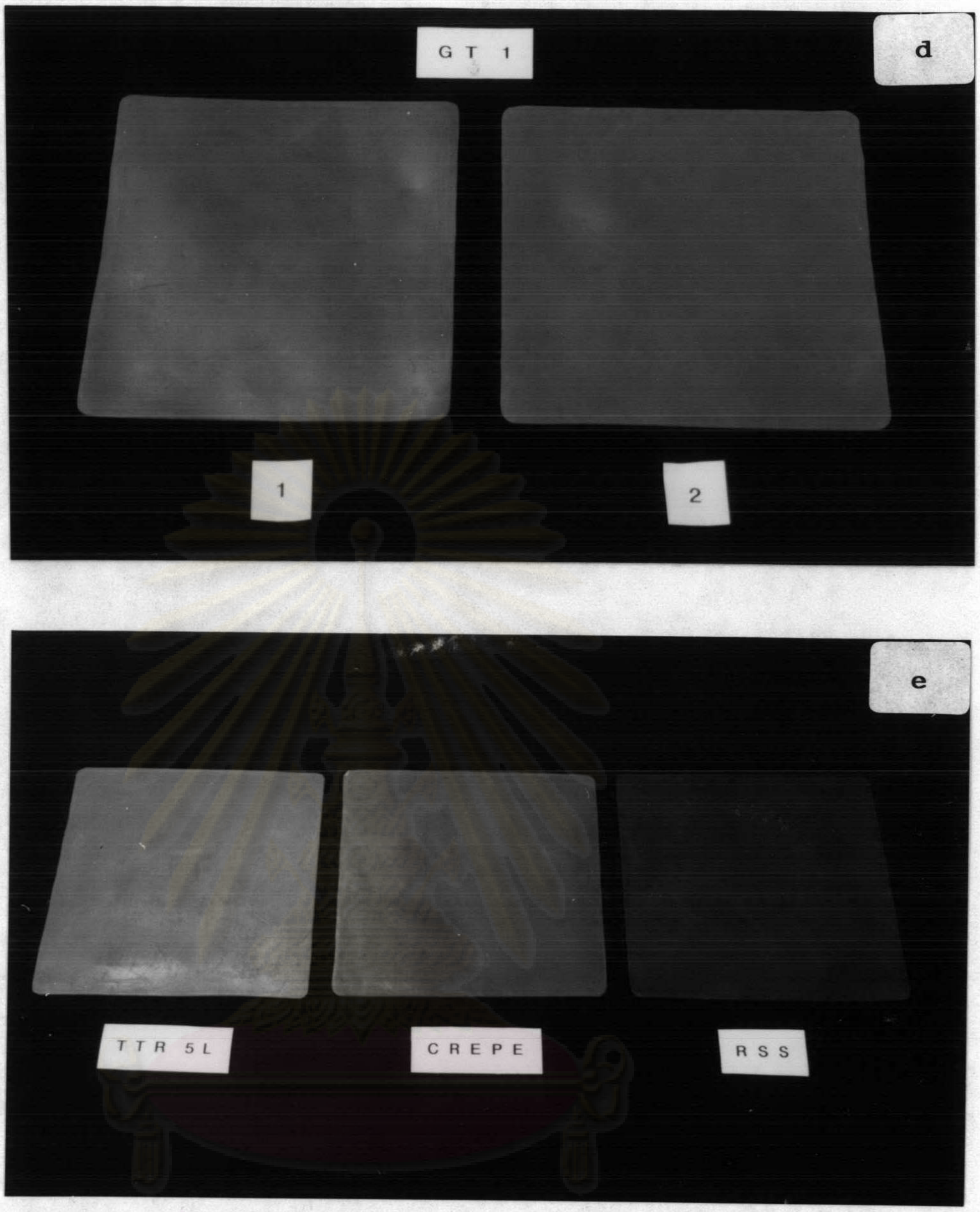

Figure 4.13 Comparison of vulcanized rubber color between CV-DPNR with its control prepared from 4 rubber clones and commercial rubber grades.

a. RRIM 600 ; b. PB 28/59 ; c. PB 5/51 ; d. GT 1 ;

e. TTR 51, white crepe and ribbed smoked sheet 1 (RSS 1)

1 Control, 2 CV-DPNR