CHAPTER 4

RESULTS AND DISCUSSION

4.1 Selection of the suitable blowing agent activator loading by thermal analysis

In this study, it has been found that the blowing agent must be evolved within a defined temperature range, which is related to the processing temperature of polymeric materials. Decomposition temperature of the pure azodicarbonamide (AZDC) is high (199 ± 1°C). Natural rubber will be degraded at this temperature. The decomposition temperature of AZDC can be made lower by adding a blowing agent activator such as zinc oxide.

The decomposition temperature of AZDC with various amounts of zinc oxide were determined by two methods. The results were then compared in order to select the best method. The two methods were:

1) Equipment setup for decomposition temperature measurement (EDTM);
2) Thermogravimetric analysis (TGA).

4.1.1 Equipment setup for decomposition temperature measurement (EDTM)

The decomposition temperature of AZDC was determined by water replacement method. The results obtained are shown in Table 4.1. It can be seen that decomposition temperature decreased significantly when 10% of zinc oxide was added. Increasing the quantity of zinc oxide, however does not appreciably reduce the decomposition temperature.

4.1.2 Thermogravimetric analysis (TGA)

TGA is used for a rapid determination of the thermal stability of substances. Essentially, by this method one measures weight loss as a function of temperature under controlled environmental conditions. TGA was used for studying the decomposition temperature of AZDC activated by various amounts of zinc oxide. During decomposition of AZDC, the weight losses were observed. In Figure 4.1 point A represents an onset of the decomposition, while B indicates the point at which the maximum rate of decomposition occurs, and point C is the temperature for the complete decomposition. The results obtained are presented in Table 4.1. It can be seen that the decomposition temperature of AZDC decreases with increasing amounts of zinc oxide. During the transformation between metallic salts (zinc oxide) and azodicarbonamide, azodicarboxylate intermediate is found and; it is less stable than azodicarbonamide.

4.1.3 Comparison of the two methods for the measurement of decomposition temperature.

Results of the measurements of decomposition temperature by the two methods are compared in Table 4.1. The concentration of zinc oxide used as an activator for AZDC was varied between 10%-100% in order to adjust the decomposition temperature of AZDC.

It can be seen from Table 4.1 that the decomposition temperature determined by EDTM and TGA show different results. The decomposition temperature of AZDC as determined by TGA is relatively higher than that measured by EDTM. This is not surprising since TGA measures weight loss accompanying the decomposition of the blowing agent. Therefore, it is more sensitive than EDTM which measures physical changes. The EDTM measures the volume of a gas evolved into a large empty space, therefore, the gas generated by the blowing agent has to fill the space in the apparatus first before detection can be made.

Table 4.1 Comparison of the two methods for the measurement of decomposition temperature

Composition	Temperature at maximum decomposition (°C)	
	EDTM	TGA
Azodicarbonamide (AZDC)	200	208.4
AZDC + 10% zinc oxide	170	197.9
AZDC + 25% zinc oxide	165	196.2
AZDC + 50% zinc oxide	163	179.3
AZDC + 75% zinc oxide	163	167.6
AZDC + 100% zinc oxide	158	164.7

Since TGA is the most sensitive and accurate method, it should be the method of choice for measurement of decomposition of the blowing agent. However, EDTM also gives reproducible results. It may be used to determine the decomposition temperature of blowing agents in factory because of simplicity and cheap to set up.

From these results, the suitable decomposition temperature of AZDC was selected to be 170 °C using AZDC with 10% zinc oxide. Since the temperature in the mixer was controlled at the softening point of the high-density polyethylene (150°C), The decomposition temperature of AZDC must be higher than the mixing temperature in order to prevent premature decomposition of AZDC.

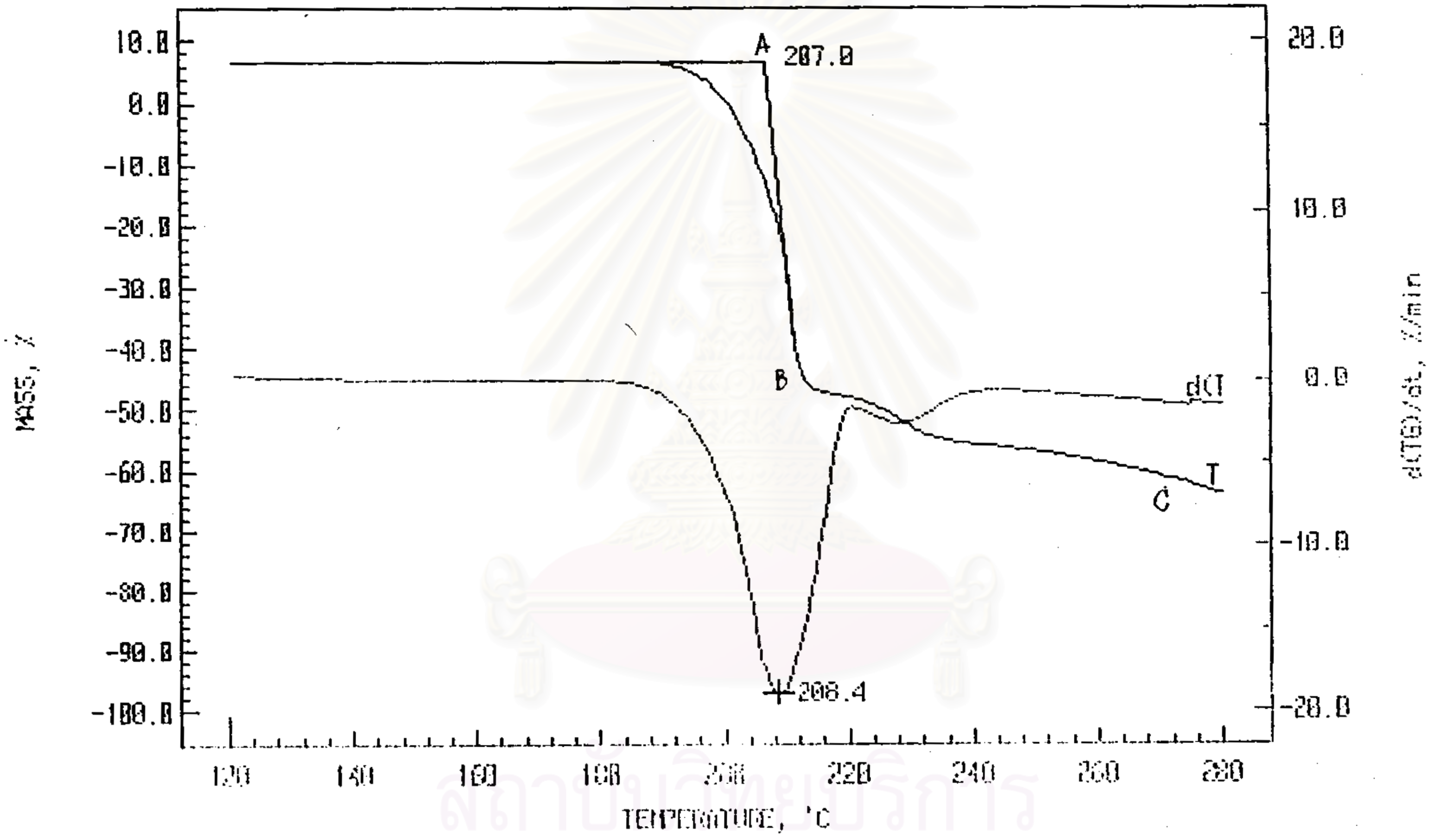
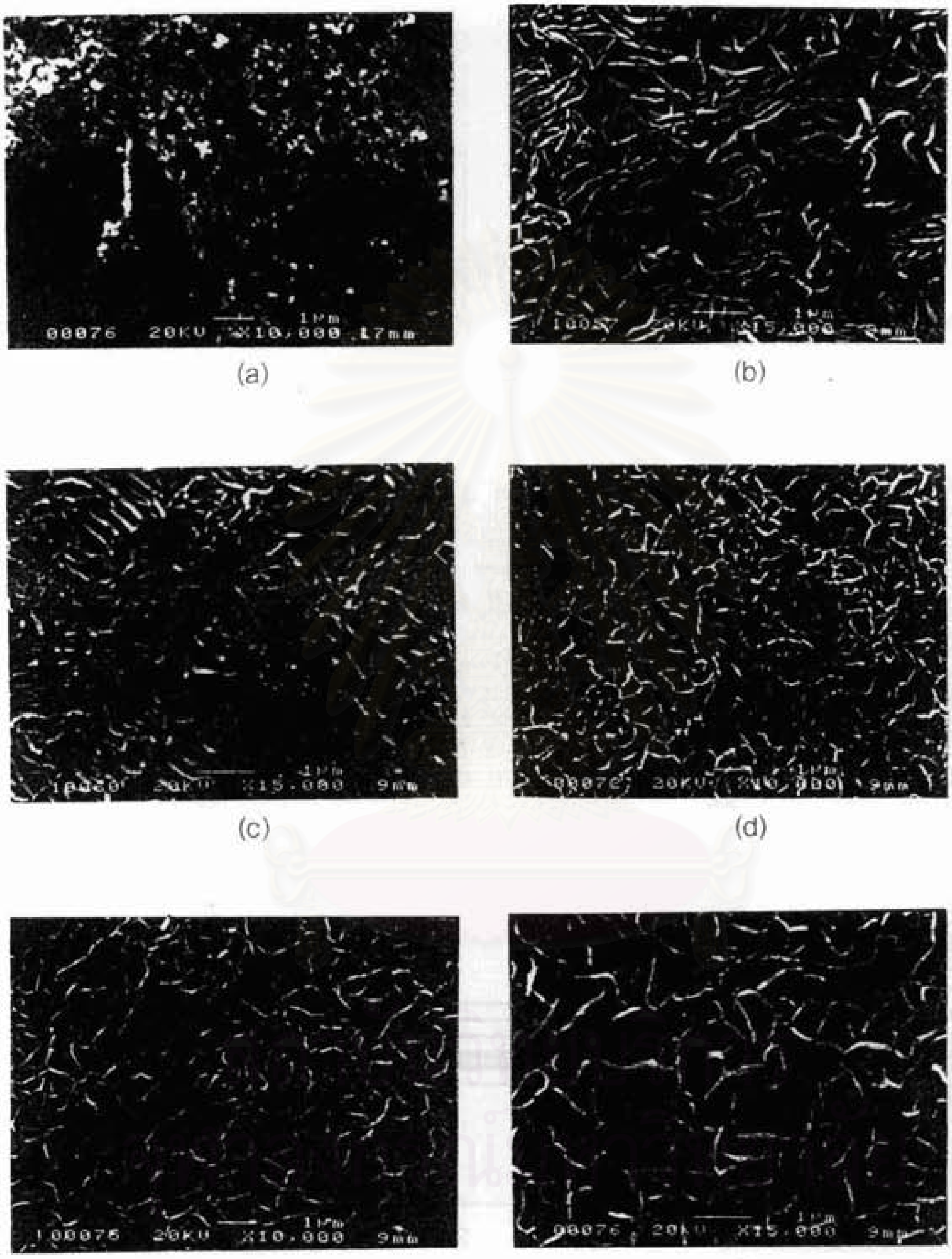


Figure 4.1 TGA thermogram of azodicarbonamide.

4.2 Determination of the distribution of natural rubber phase in high-density polyethylene phase

The distribution of natural rubber phase in high-density polyethylene phase was determined by scanning electron microscopy. The series C formulation was studied. The scanning electron micrograph of toluene extracted 100-HDPE, and the extracted blends of 90/10 HDPE/NR, 80/20 HDPE/NR, 70/30 HDPE/NR, 60/40 HDPE/NR, and 50/50 HDPE/NR are shown in Figures 4.2 (a)-(f), respectively. Almost all structures of the micrographs consist of white threads or the plastic network and dark areas except structure of 100-HDPE. The dark areas correspond to the empty holes left behind by the NR after dissolving in toluene, and the white threads or the plastic network areas represent the un-etched high-density polyethylene. It is apparent that the dark areas increases in size with increasing the NR content (Figures 4.2 (b) - (f)) and the distribution of NR in HDPE phase is relatively uniform. The uniformity of NR in HDPE phase is shown in Figure 4.3. It can be seen that the high quantity of threads width was 0.62 mm in every percentage of NR content.



(a) (b)

(c) (d)

(e) (f)

Figure 4.2 SEM micrographs of toluene extracted blends: (a) 0 pphp NR, (b) 10 pphp NR, (c) 20 pphp NR, (d) 30 pphp NR, (e) 40 pphp NR, and (f) 50 pphp NR (series C)

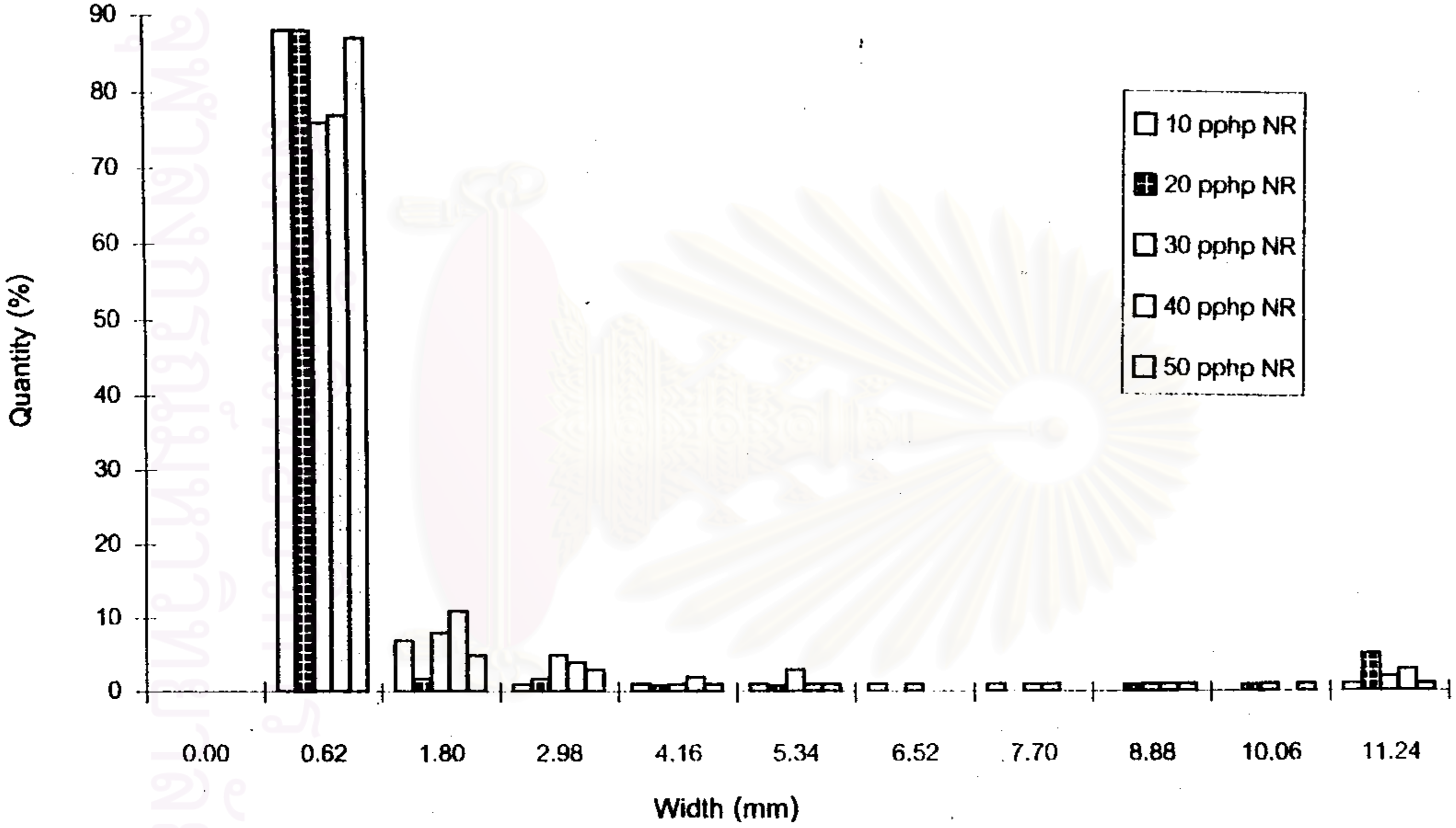


Figure 4.3 The distribution of threads width from SEM micrographs

4.3 Factors affecting the dynamic mechanical properties of HDPE/NR foams

Dynamic mechanical tests, in general, give more information about a material than do other tests. Dynamic mechanical tests over a wide temperature range are especially sensitive to transitions, morphological changes, and structural change in polymers. Types of useful information that can be obtained from dynamic mechanical tests include glass transition temperature (Tg), secondary transitions, miscibility of polymer blends, and morphology.

4.3.1 Effect of HDPE/NR ratio

The effect of HDPE/NR ratio on the dynamic mechanical properties of HDPE/NR foams in series C was studied by varying the ratios of HDPE/NR blends between 90/10 and 50/50 in 2 pphp of the blowing agent loading.

The dynamic mechanical spectra of 90/10, 80/20, 70/30, 60/40 and 50/50 of HDPE/NR blends are shown in Figures 4.4-4.8 respectively. There are three regions of mechanical behavior that can be distinguished as follows (see Figure 4.6):

i) a glassy region.

ii) a glass-rubber or a viscoelastic region and

iii) a rubbery region.

The viscoelastic region increased with increasing NR content. The DMA data also shows the presence of separated HDPE and NR phase in all blends indicated by the existence of two Tg's belonging to HDPE and NR (see Table 4.2). The results are shown in Figures 4.4 and 4.5 for 90/10 HDPE/NR and 80/20 HDPE/NR blend, respectively. However, the Tg of HDPE was not detected in 70/30, 60/40 and 50/50 HDPE/NR blends. It was understood that these blends exhibit a two-phased structure since the Tg observed was the characteristic Tg of NR (Tg's the pure natural rubber as -50°C)[30]. Intermediate Tg would have been observed if a significant inter-polymer mixing occurs. When NR is content more than 20 pphp it becomes soft materials; some difficulties were then faced in loading and clamping the samples. Tg was unable to be detected for high NR containing samples. All blend ratios show a drop in the storage modulus due to the elastic nature of NR (indicated by the lower Tg). The drop in the storage modulus with temperature during the transition from the glassy state to the rubbery state is progressively steeper with increasing rubber content. The loss modulus is roughly estimated for all the blend ratios as close to the NR glass transition temperature. The loss tangent increases sharply with the increasing rubber content in the blends.

Table 4.2 Effect of HDPE/NR ratio on the dynamic mechanical properties of HDPE/NR foam

HDPE/NR ratio	Tg (°C)		Modulus (Pa x 10^9)			
	Tg_1	Tg_2	storage at		loss at	
	(HDPE)	(NR)	Tg_1	Tg_2	Tg_1	Tg_2
90/10	-84.6	-30.2	3.6	2.6	0.1	0.1
80/20	-91.7	-34.5	1.3	0.7	0.1	0.1
70/30	-	-28.0	-	2.8	-	0.5
60/40	-	-29.6	-	0.5	-	0.1
50/50	-	-25.9	-	0.3	-	0.1

4.3.2 Effect of blowing agent loading

The effect of blowing agent loading on the cell structure and properties of HDPE/NR foams of series B was studied by varying the blowing agent loading between 1.0 and 5.0 pphp

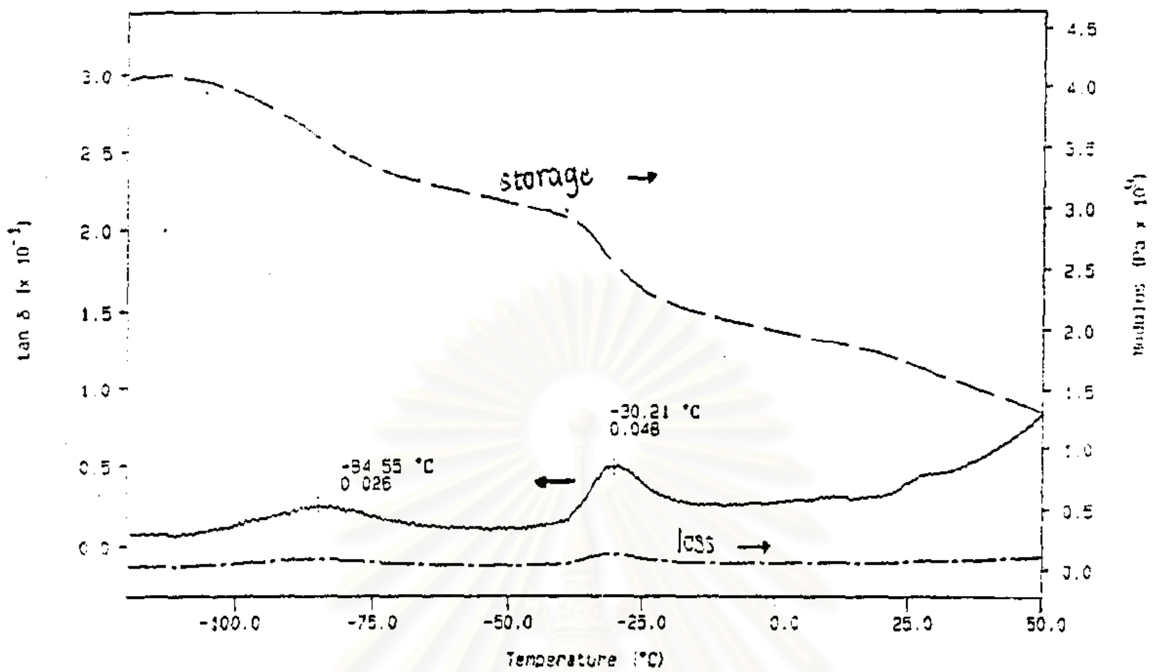


Figure 4.4 Dynamic mechanical spectra of HDPE/NR foam at 10 pphp NR content

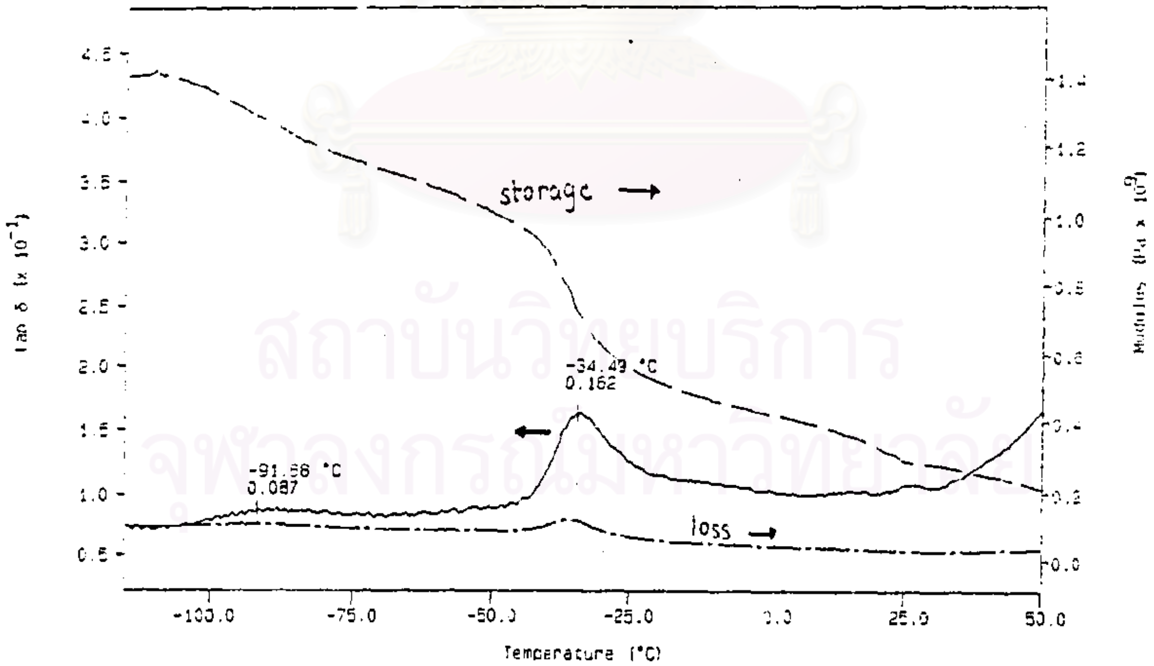


Figure 4.5 Dynamic mechanical spectra of HDPE/NR foam at 20 pphp NR content

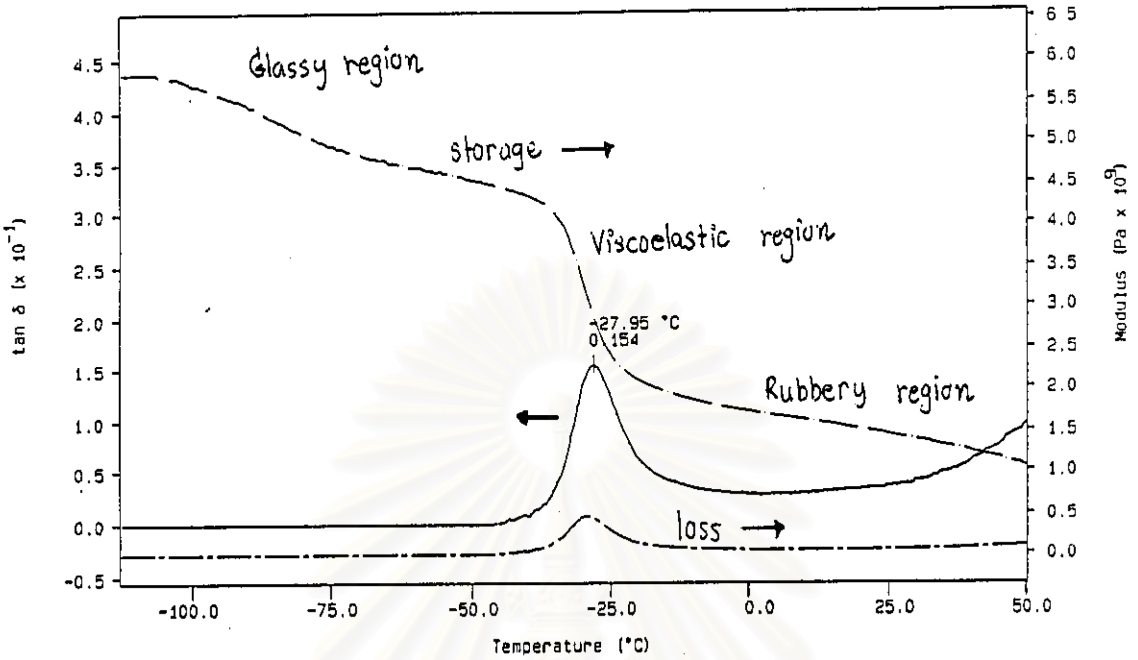


Figure 4.6 Dynamic mechanical spectra of HDPE/NR foam at 30 pphp NR content

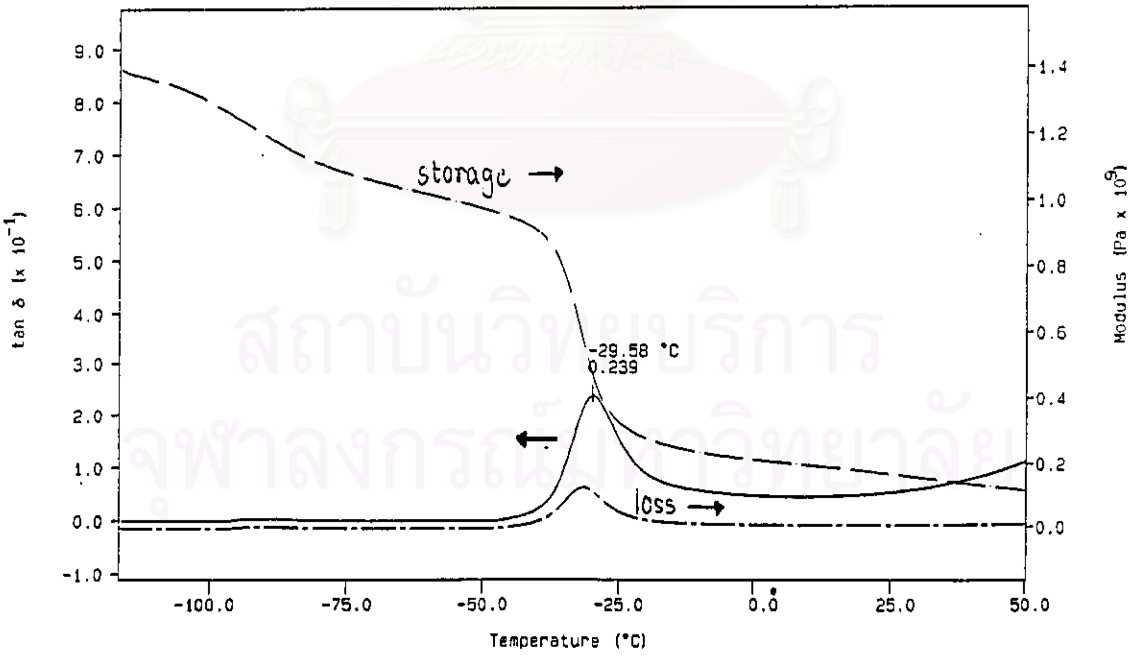


Figure 4.7 Dynamic mechanical spectra of HDPE/NR foam at 40 pphp NR content

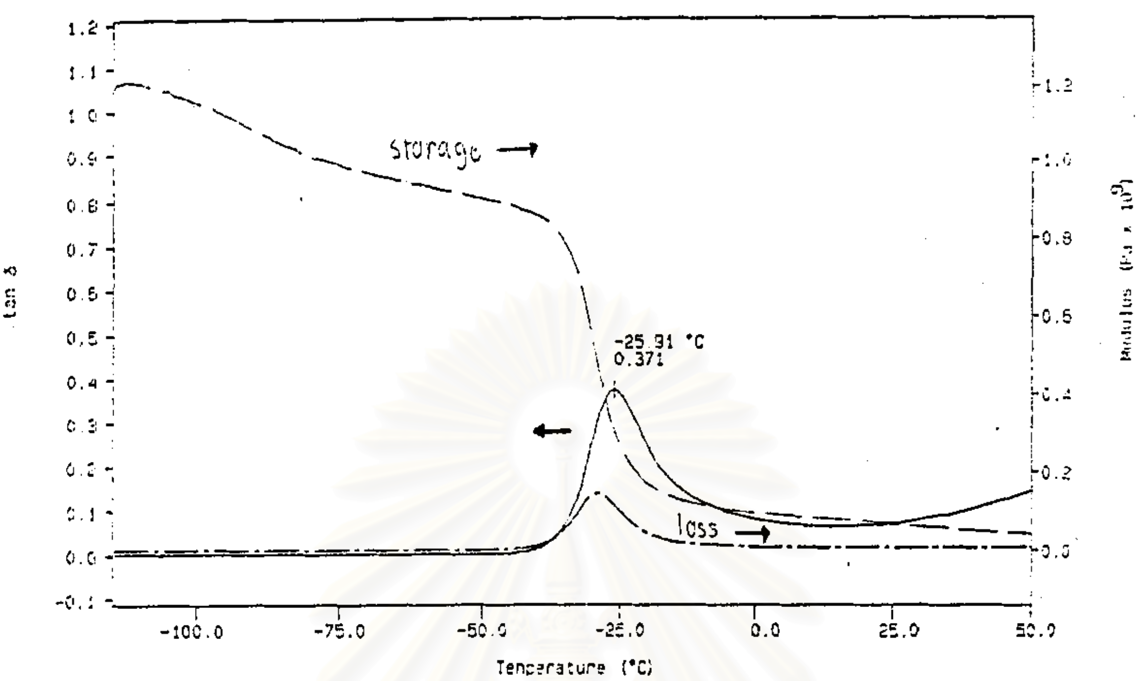


Figure 4.8 Dynamic mechanical spectra of HDPE/NR foam at 50 pphp NR content

The dynamic mechanical spectra of 1 pphp, 2 pphp, 3 pphp, 4 pphp and 5 pphp of the blowing agent loading are shown in Figure 4.9-4.13 respectively. There are also three regions of mechanical behavior, which can be distinguished as follows (see Figure 4.9)

i) a glassy region.
ii) a glass-rubber or a viscoelastic region and
iii) a rubbery region.

Considering the dynamic mechanical spectra, there are two Tg corresponding to Tg of NR and HDPE which were obtained at about -30°C and about -89°C respectively (see Table 4.3). Such data could not be used to identify any difference of blowing agent loading in HDPE/NR foam. Therefore, the DMTA could not be used to follow the quality of HDPE/NR foams as required.

Table 4.3 Effect of blowing agent loading on the dynamic mechanical properties of HDPE/NR foam

Blowing agent loading (pphp)	Tg (°C)		Modulus (Pa x 10^9)			
	Tg_1 (HDPE)	Tg_2 (NR)	storage at		loss at	
			Tg_1	Tg_2	Tg_1	Tg_2
1.0	-89.8	-32.7	1.1	0.6	0.1	0.1
2.0	-91.7	-34.5	1.3	0.7	0.1	0.1
3.0	-88.2	-34.0	1.0	0.5	0.0	0.1
4.0	-85.1	-24.2	1.0	0.5	0.1	0.1
5.0	-	-25.8	-	1.1	-	0.1

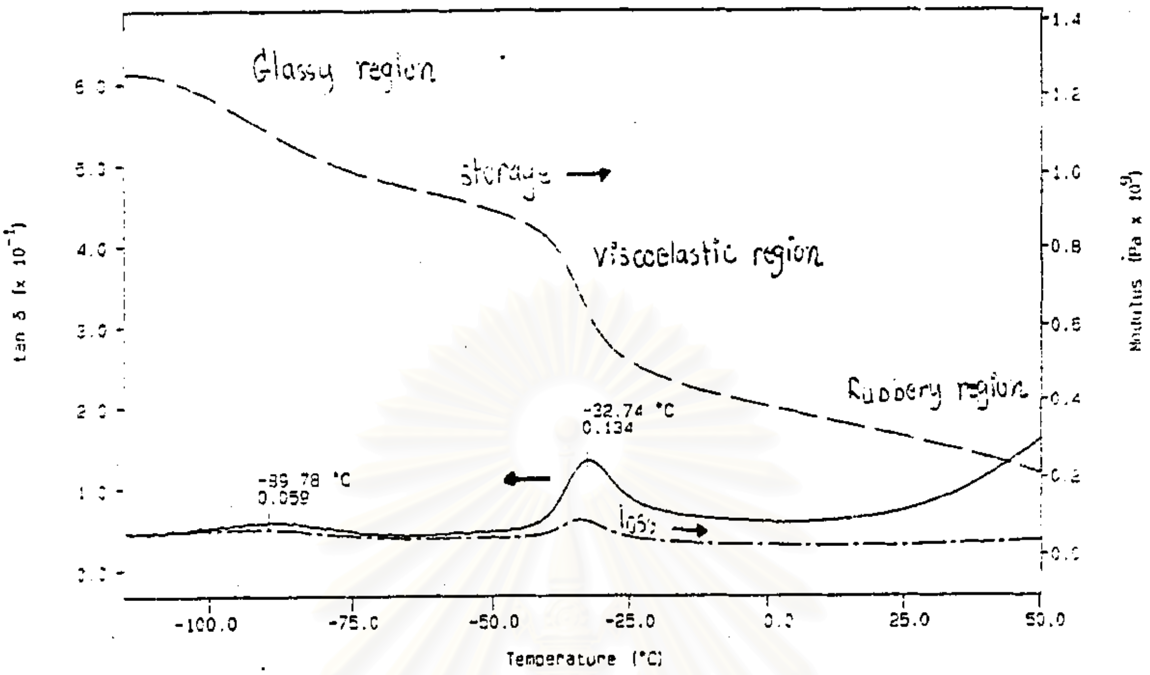


Figure 4.9 Dynamic mechanical spectra of HDPE/NR foam at 1.0 pphp blowing agent

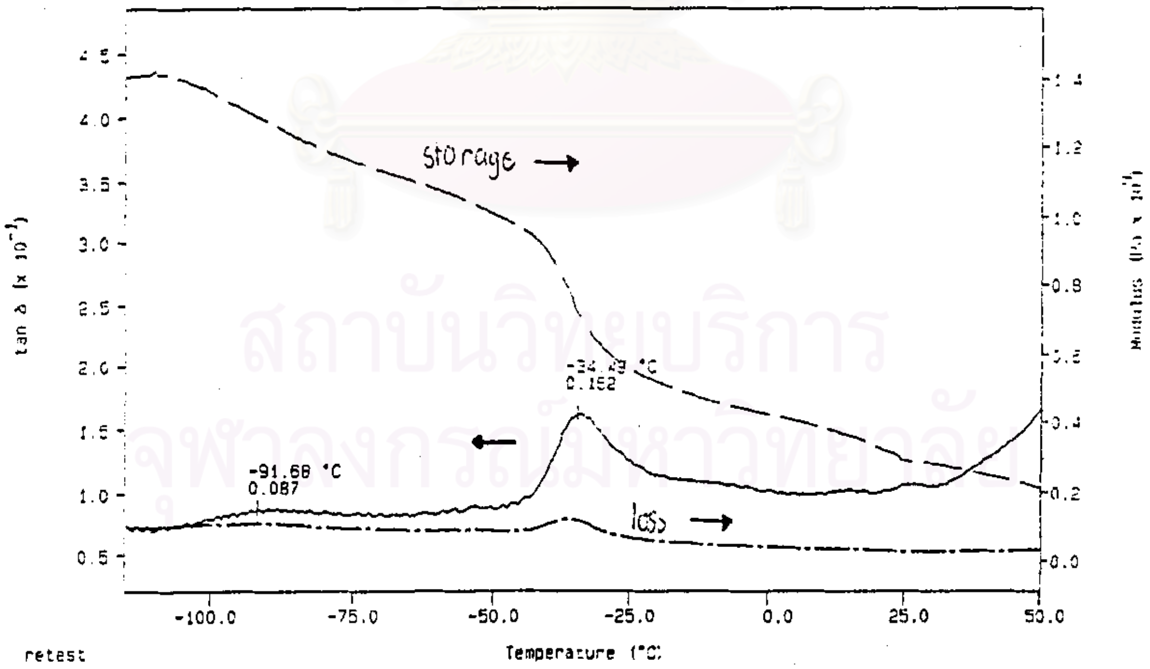


Figure 4.10 Dynamic mechanical spectra of HDPE/NR foam at 2.0 pphp blowing agent

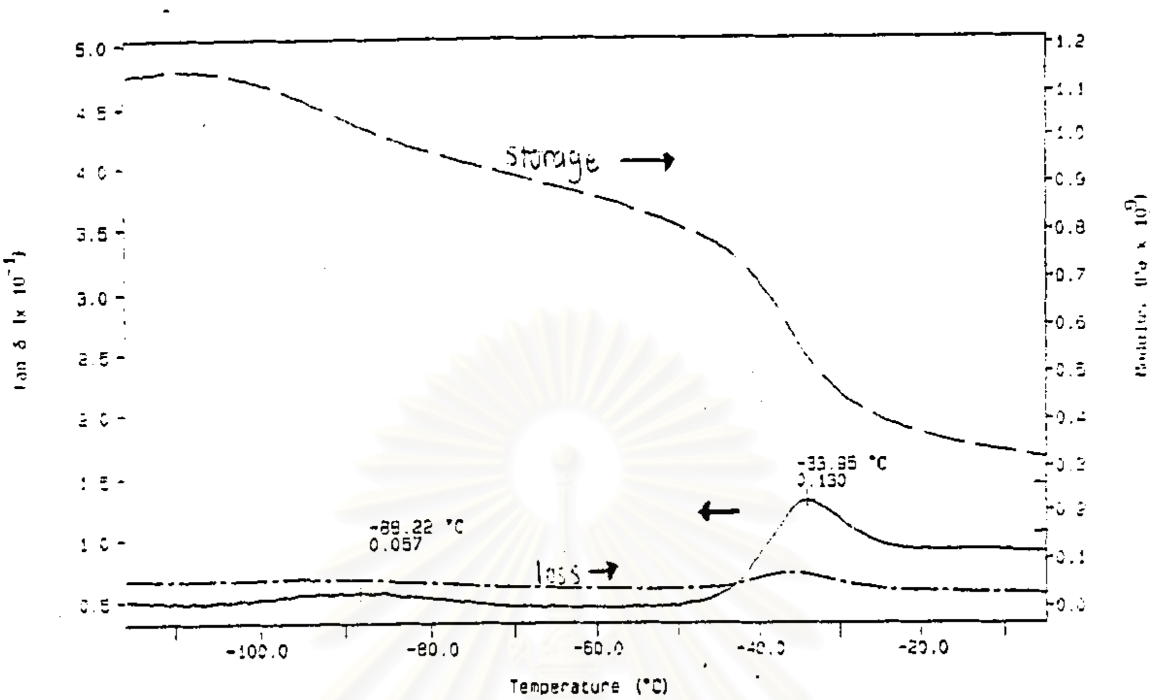


Figure 4.11 Dynamic mechanical spectra of HDPE/NR foam at 3.0 pphp blowing agent

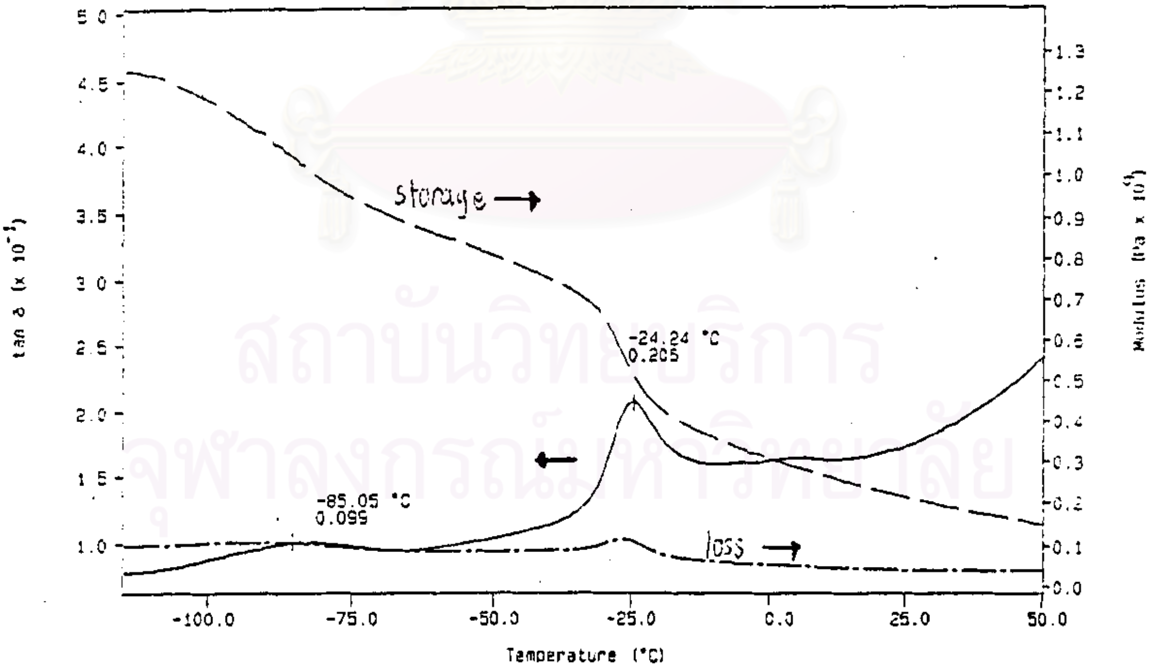


Figure 4.12 Dynamic mechanical spectra of HDPE/NR foam at 4.0 pphp blowing agent

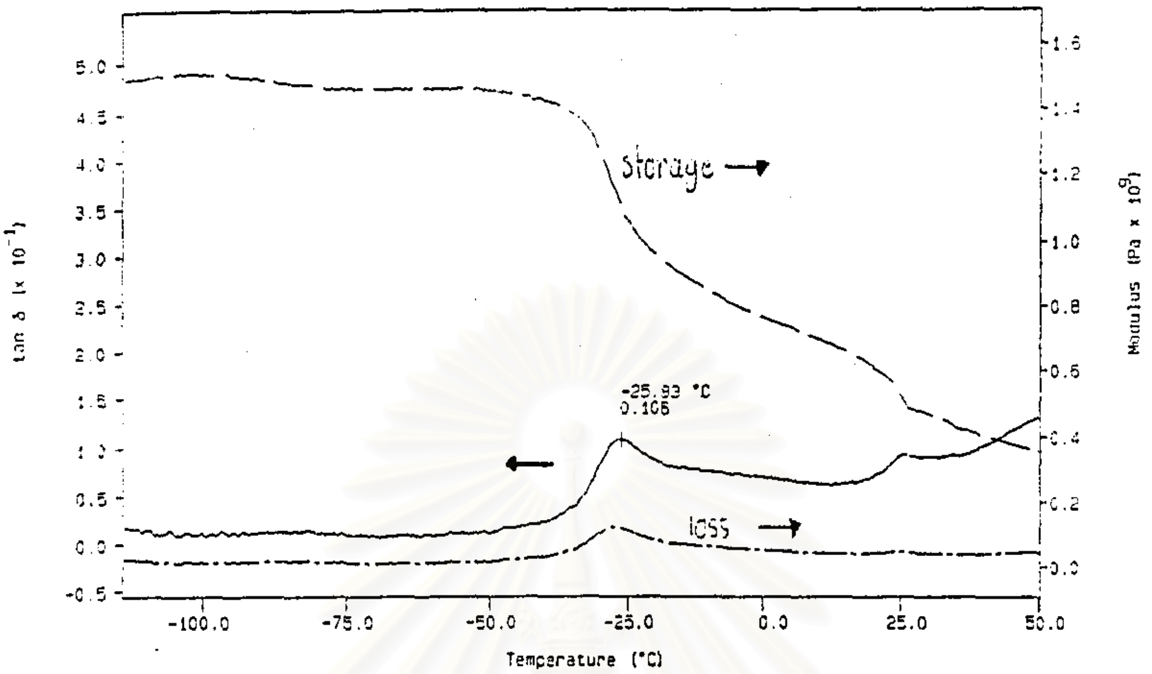


Figure 4.13 Dynamic mechanical spectra of HDPE/NR foam at 5.0 pphp blowing agent

4.4 Factors affecting the cell structure and mechanical properties of HDPE/NR foams

4.4.1 Effect of heating time

The effect of heating time on the cell structure and mechanical properties of HDPE/NR foams in series A formulation was studied. The heating time was varied from 10 to 30 minutes at 170 °C, with a five-minute increment.

The results are shown in Table 4.4 and Figures 4.14-4.22. From Figure 4.14, it can be seen that foam density decreases with increasing heating time and approaches a constant values after 20 minutes of heating time. This indicates a complete decomposition of the chemical blowing agent, AZDC. Three physical changes usually take place during the foaming process. First, exothermic heat is evolved from the decomposition reaction of the blowing agent. Second, the loss in weight of the blowing agent due to evolution of gas. Finally, the matrix is expanded by internal pressure of the evolved gases leading to a dimensional change. The values of hardness, tensile strength, elongation at break, tear strength and elastic modulus decreases with increasing heating time, show in Figures 4.15-4.18 and Figure 4.20. The longer heating time released more gas than shorter heating time. The increasing gas phase resulted in the decrease in numerical value of those properties. In addition, it can be explained by the structure of the foams. From Table 4.4, the foam formed by a 10-minutes heating time produces the larger average cell size (~0.5 mm) than that of longer heating times (>10 minutes)(~0.4 mm). The quantity of cell per area of the shorter heating time was less than those of the longer heating time. Therefore, the cell struts of shorter heating time was expected to be thicker than those of the longer heating times.

Based on these results 20 minutes of the heating time has been used for further investigation. This is because the blowing agent decomposes completely as indicated by the foam density.

Table 4.4 Effect of heating time on the cell structure and mechanical properties of HDPE/NR foams.

Cell structure & mechanical properties	Heating time (min)				
	10	15	20	25	30
Average cell size (mm)	0.51	0.40	0.40	0.43	0.46
Cell size distribution (mm)	0.12	0.07	0.09	0.10	0.13
Maximum cell size (mm)	0.85	0.57	0.70	0.72	0.94
Minimum cell size (mm)	0.25	0.21	0.21	0.21	0.21
Foam density (g/cm^3)	0.78	0.66	0.57	0.50	0.51
Hardness shore (A)	35±0	34±1	33±1	33±1	33±1
Tensile strength (MPa)	2.3±0.3	1.8±0.1	1.4±0.3	1.3±0.1	1.0±0.1
Elongation at break (%)	112±38	170±59	115±43	131±19	69±23
Tear strength (kN/m)	68.1±3	66.3±4	46.7±4	42.1±3	32.1±3
Flexural strength (MPa)	5.6±0.2	5.9±0.4	5.5±0.2	5.0±0.1	5.0±0.3
Elastic modulus (MPa)	192±18	239±43	155±19	139±6	127±16

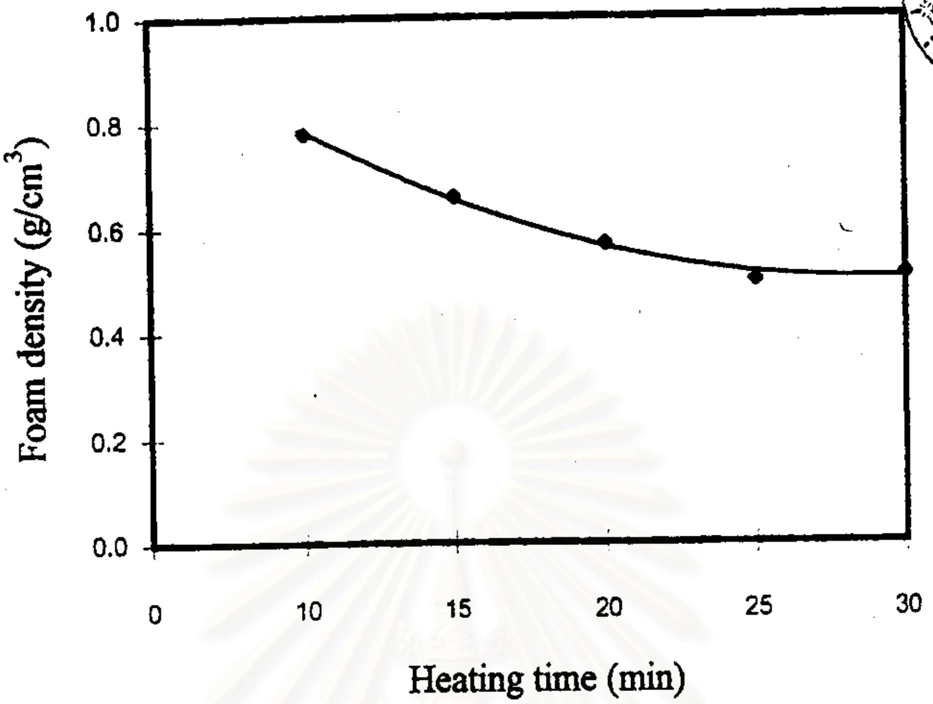


Figure 4.14 Effect of heating time on foam density

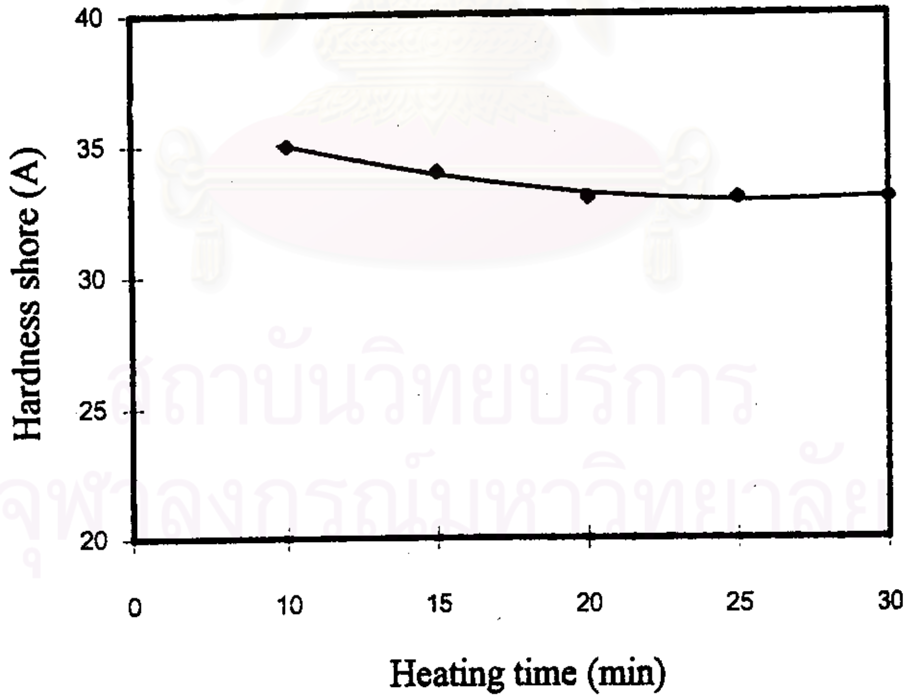


Figure 4.15 Effect of heating time on hardness

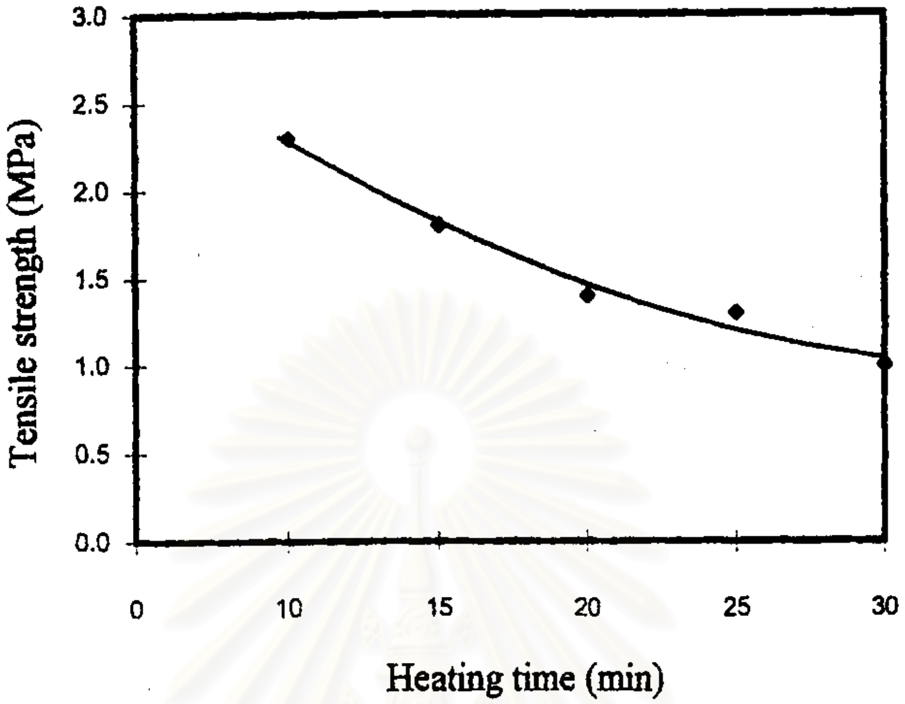


Figure 4.16 Effect of heating time on tensile strength

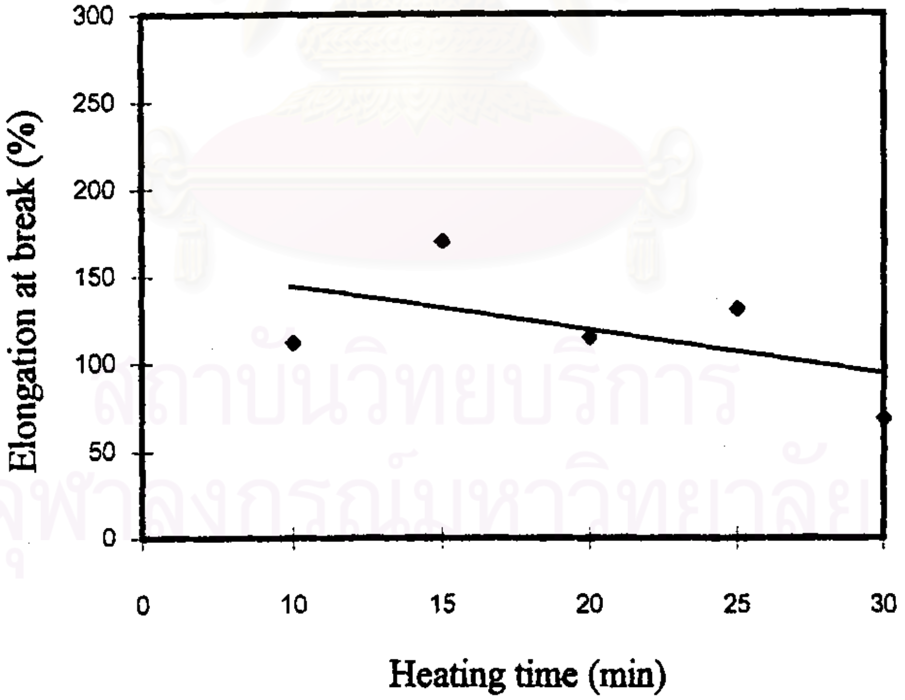


Figure 4.17 Effect of heating time on elongation at break

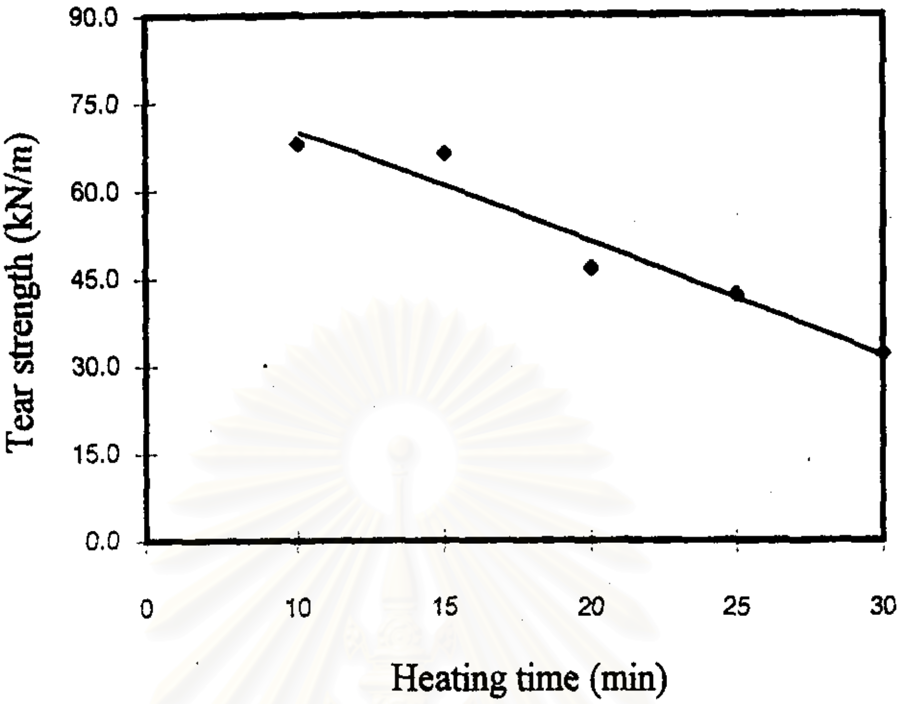


Figure 4.18 Effect of heating time on tear strength

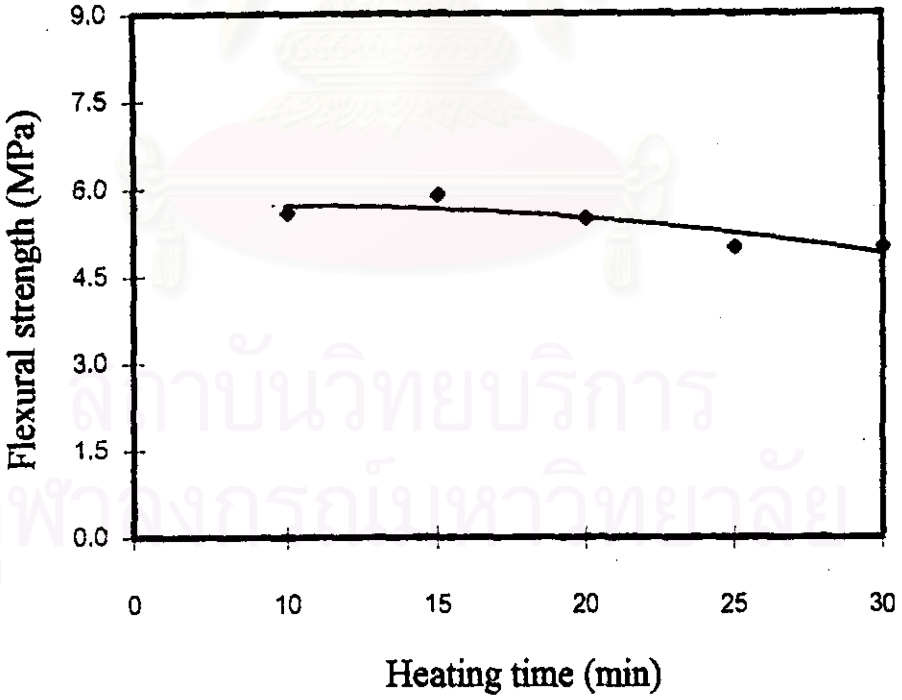


Figure 4.19 Effect of heating time on flexural strength

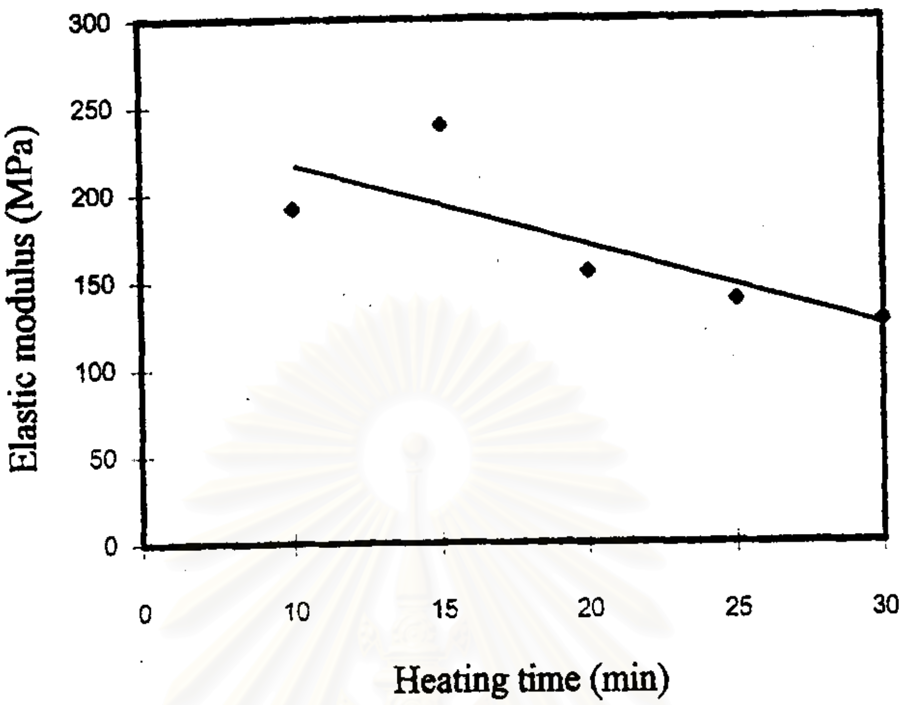
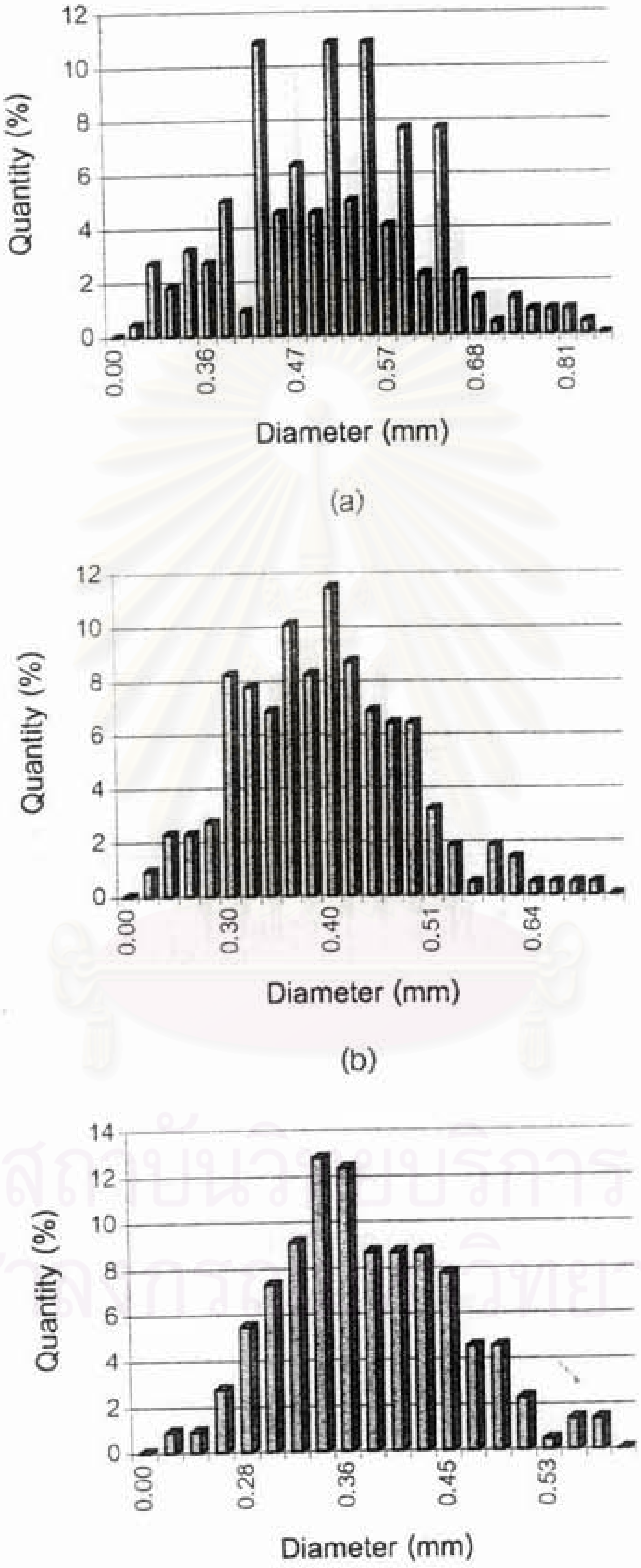
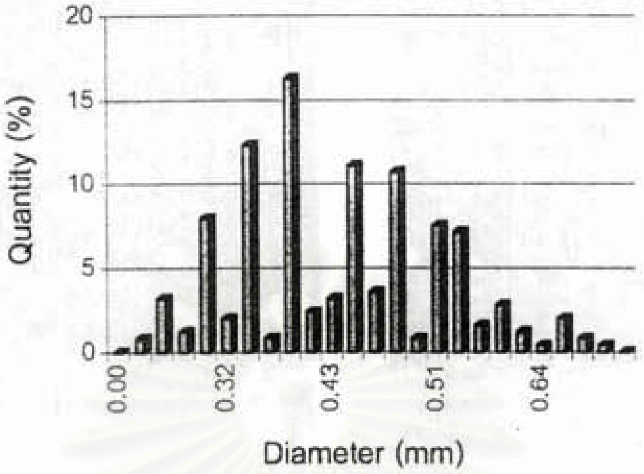


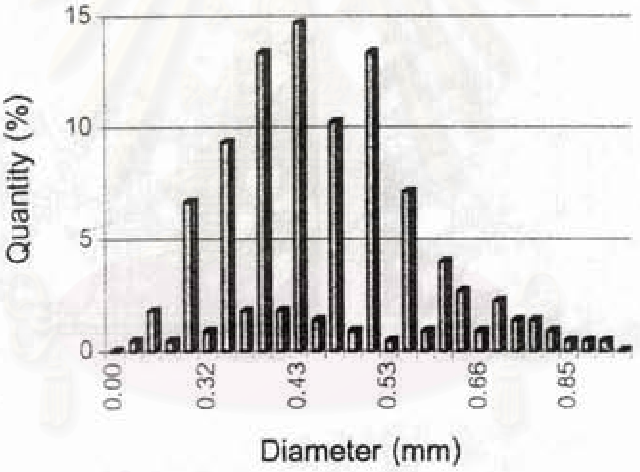
Figure 4.20 Effect of heating time on elastic modulus


12
10
8
6
4
2
0
Quantity (%)
0.00
0.36
0.47
0.57
0.68
0.81
Diameter (mm)
(a)
12
10
8
6
4
2
0
Quantity (%)
0.00
0.30
0.40
0.51
0.64
Diameter (mm)
(b)
14
12
10
8
6
4
2
0
Quantity (%)
0.00
0.28
0.36
0.45
0.53
Diameter (mm)

(c)



(d)



(e)

Figure 4.21 The effect of heating time on cell size distribution of HDPE/NR foam (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min, and (e) 30 min (series A)

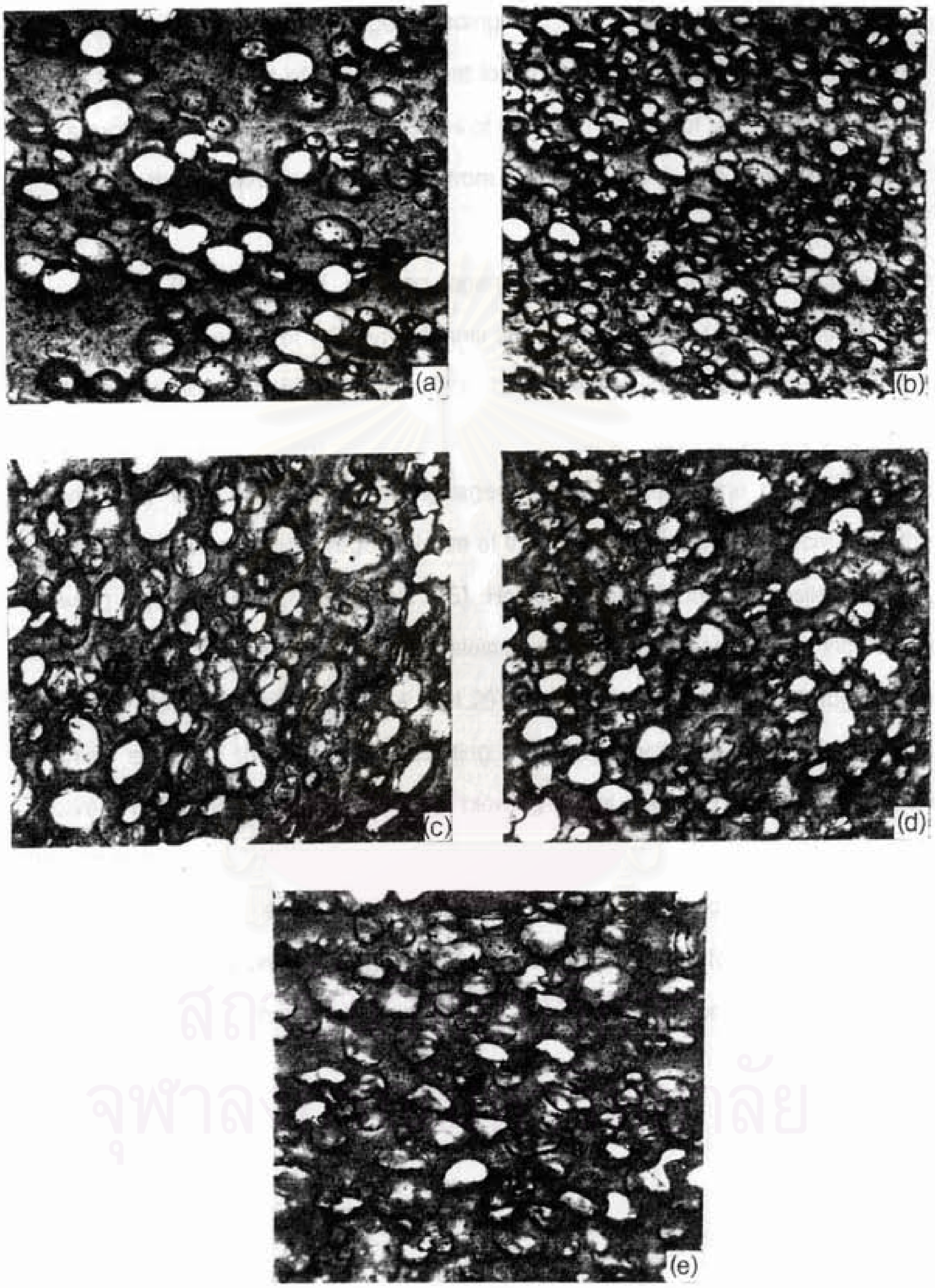


Figure 4.22 The effect of heating time on cell structures of HDPE/NR foam (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min, and (e) 30 min (series A)

4.4.2 Effect of blowing agent loading

The effect of blowing agent loading at 20 minute heating time on the cell structure and mechanical properties of HDPE/NR foams of series B was studied by varying the blowing agent loading from 1.0 to 5.0 pphp with a one-percentage increment.

The effect of blowing agent loading on the cell structure and mechanical properties of HDPE/NR foams are given in Table 4.5 and Figures 4.23-4.31 The blowing agent content affects both the cell structure and mechanical properties of HDPE/NR foams. It can seen form Figure 4.33, the density decreases appreciably with increasing blowing agent loading due to the quantity of gas released. Likewise, the average cell size of the foams increased with increasing the blowing agent loading, (see Table 4.5). However, the hardness, tensile strength, tear strength, flexural strength and elastic modulus decreases with increasing weight of blowing agent (Figures 4.23-4.25 and Figures 4.27-4.29), probably due to thinning effect of the cell walls resulting from larger volumes of the blown gas evolved. From Figure 4.26 shows that blowing agent loading has a little effect on the elongation at break.

Therefore, the suitable blowing agent loading to be employed was depends on the desired density and application of HDPE/NR foam. In this study, a 2 pphp loading of the blowing agent has been selected for further experiment.

Table 4.5 Effect of blowing agent loading on the cell structure and mechanical properties of HDPE/NR foams.

Cell structure & mechanical properties	Blowing agent loading (pphp)				
	1.0	2.0	3.0	4.0	5.0
Average cell size (mm)	0.41	0.40	0.44	0.59	0.55
Cell size distribution (mm)	0.08	0.09	0.10	0.16	0.13
Maximum cell size (mm)	0.66	0.70	0.74	1.04	0.91
Minimum cell size (mm)	0.19	0.21	0.23	0.34	0.23
Foam density (g/cm^3)	0.59	0.57	0.50	0.43	0.45
Hardness shore (A)	34±1	33±1	31±1	30±0	30±0
Tensile strength (MPa)	1.7±0.1	1.4±0.4	1.1±0.1	1.1±0.2	1.2±0.1
Elongation at break (%)	118±21	115±43	124±11	126±14	81±7
Tear strength (kN/m)	69.4±6	46.7±4	37.3±3	32.1±6	32.5±6
Flexural strength (MPa)	6.1±0.2	5.5±0.2	4.8±0.4	4.3±0.2	4.1±0.4
Elastic modulus (MPa)	239±22	155±19	142±37	110±5	114±18

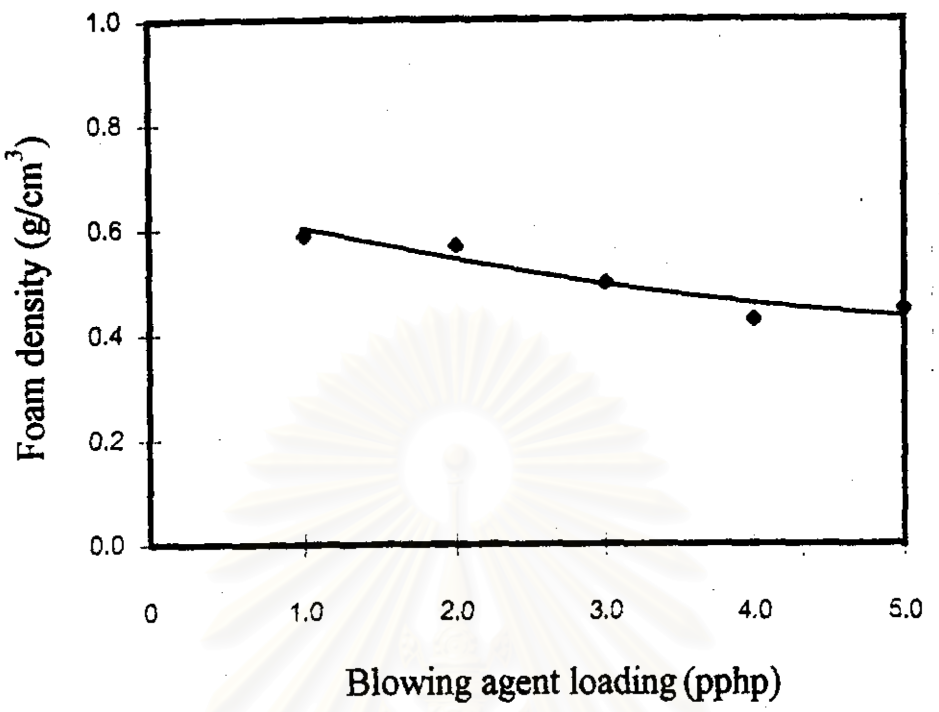


Figure 4.23 Effect of blowing agent loading on foam density

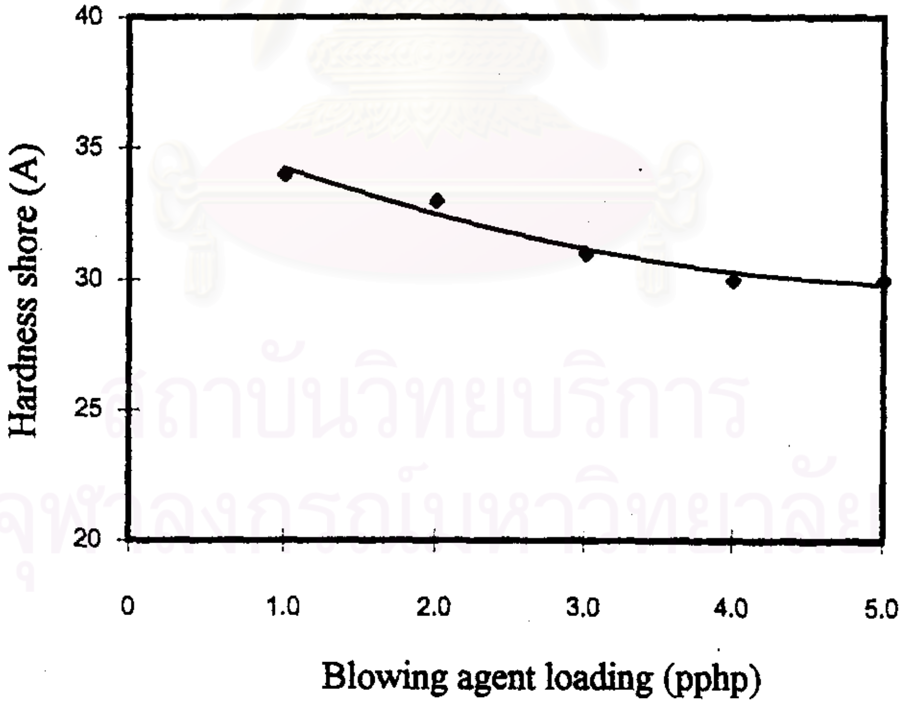


Figure 4.24 Effect of blowing agent loading on hardness

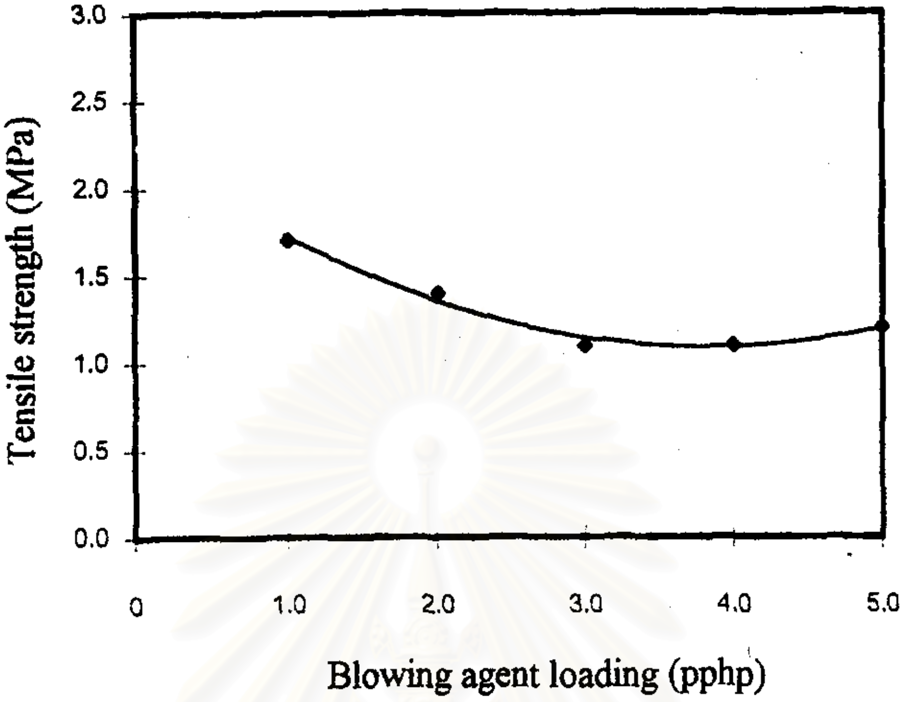


Figure 4.25 Effect of blowing agent loading on tensile strength

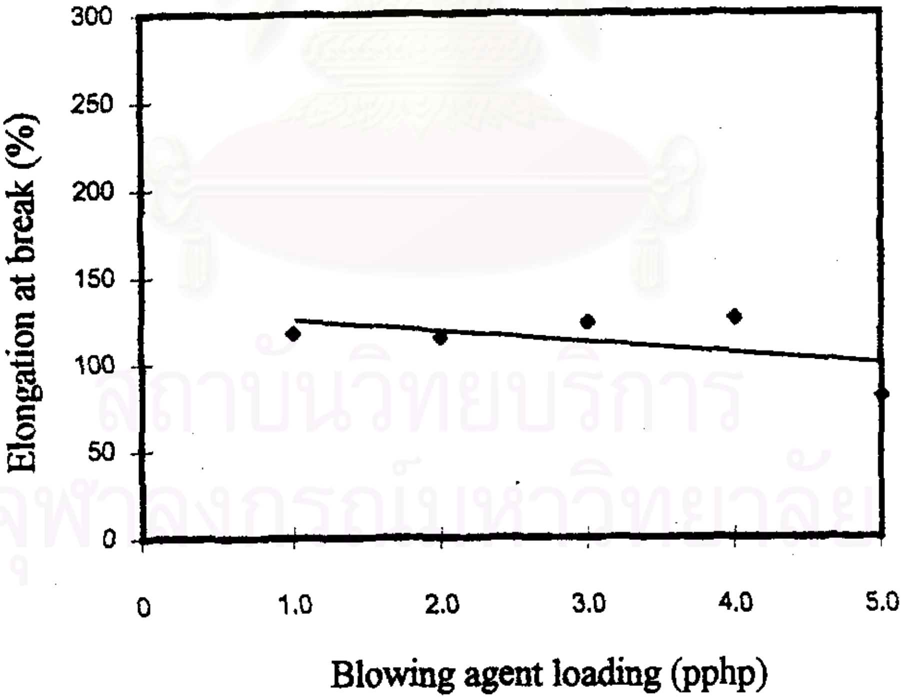


Figure 4.26 Effect of blowing agent loading on elongation at break

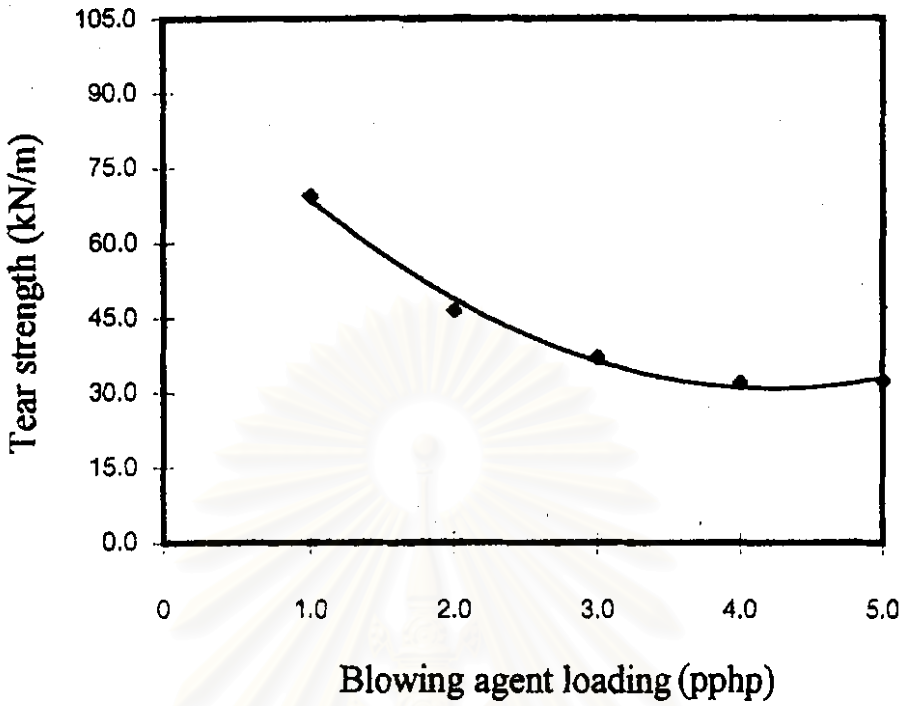


Figure 4.27 Effect of blowing agent loading on tear strength

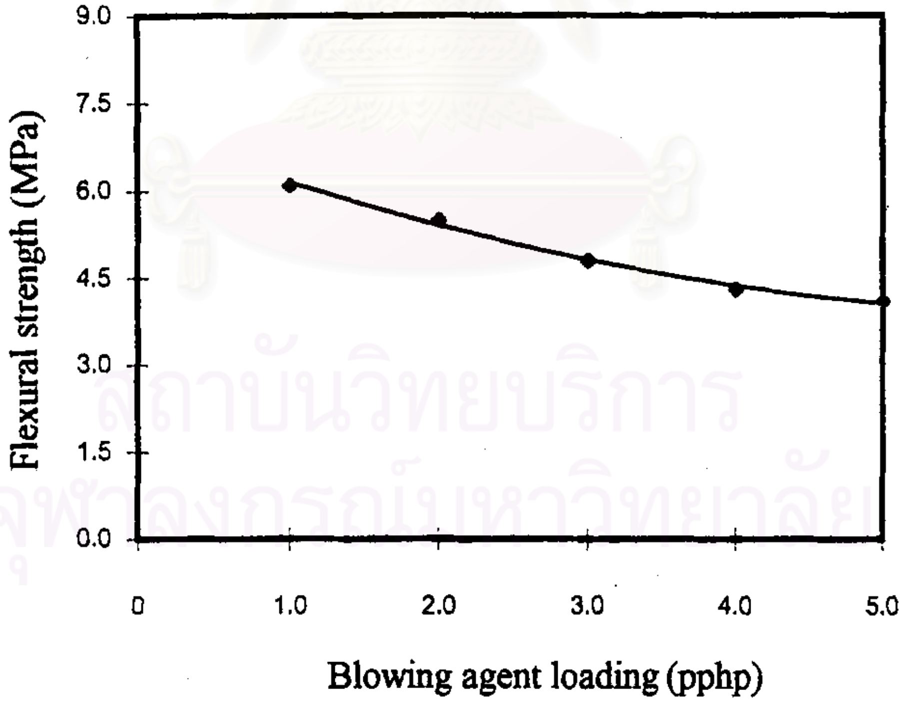


Figure 4.28 Effect of blowing agent loading on flexural strength

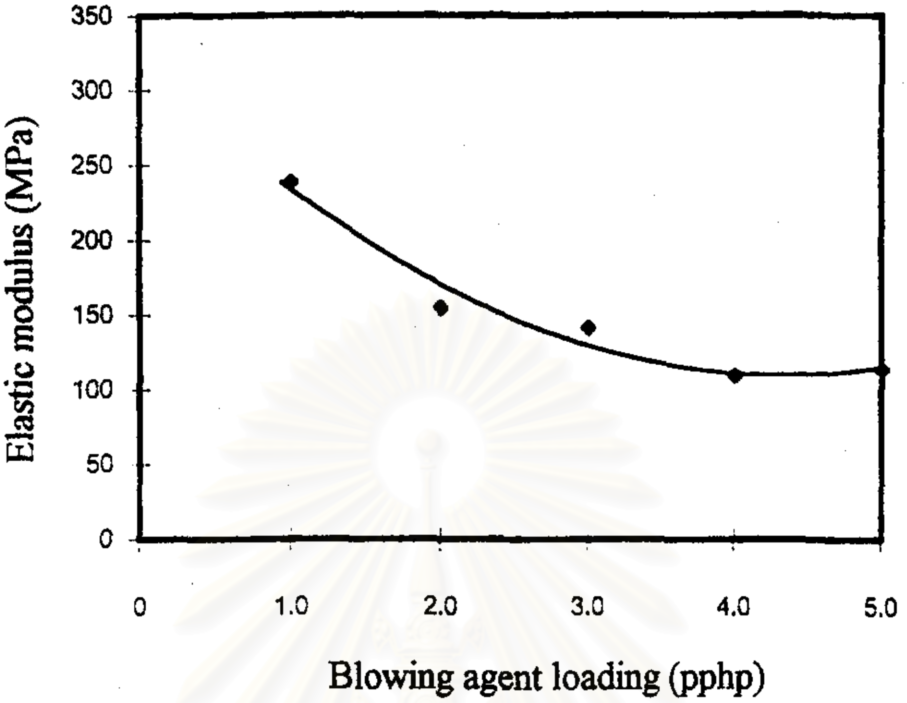
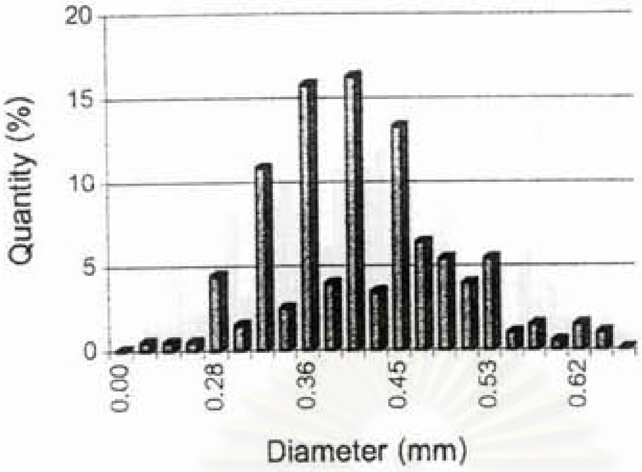
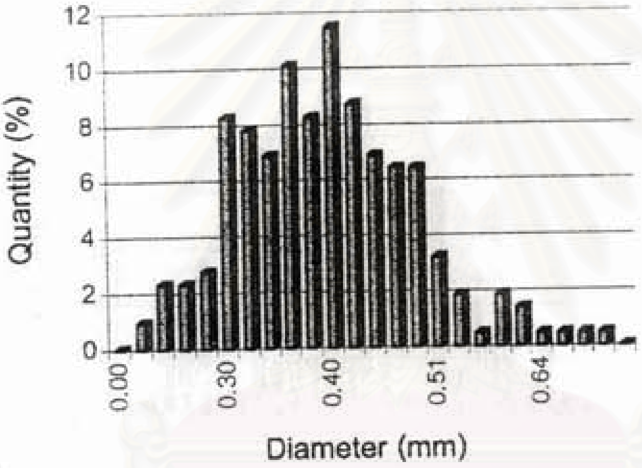


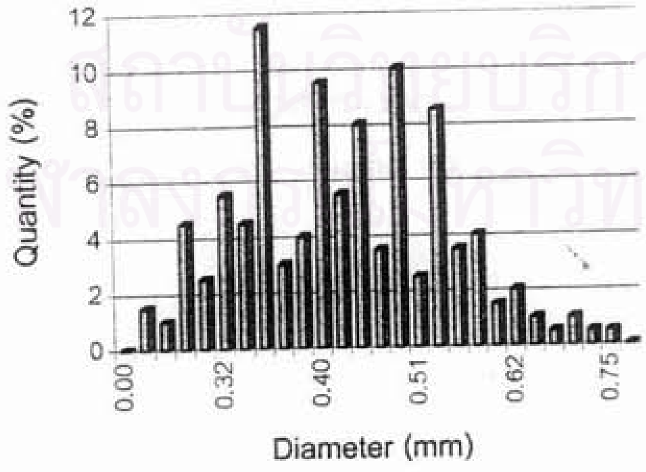
Figure 4.29 Effect of blowing agent loading on elastic modulus


Quantity (%)
20
15
10
5
0
0.00
0.28
0.36
0.45
0.53
0.62
Diameter (mm)

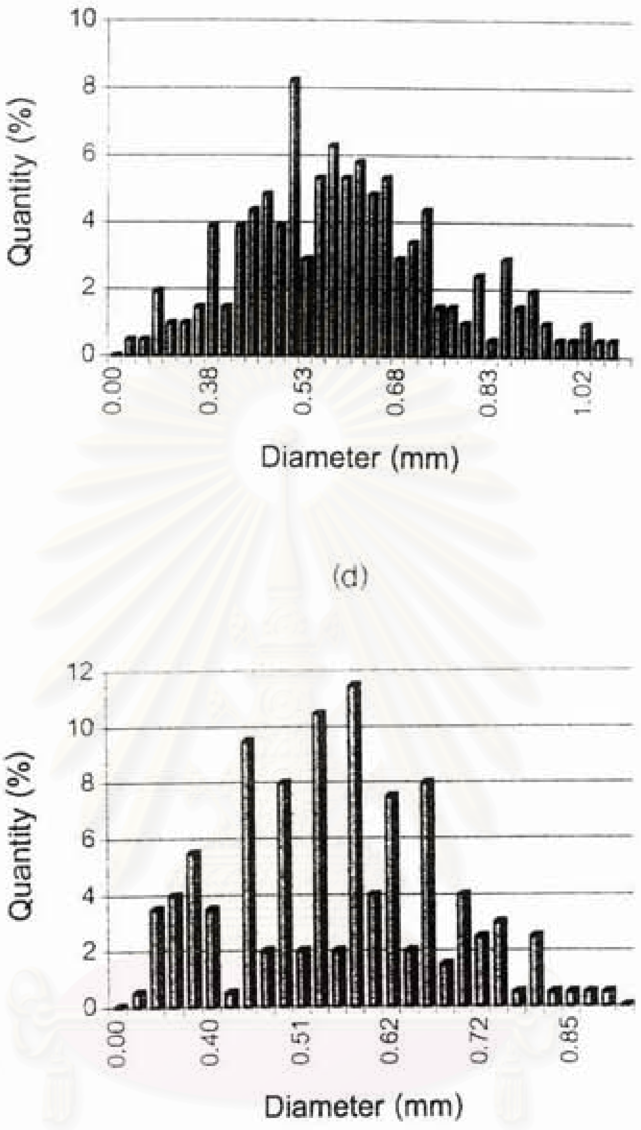
(a)


Quantity (%)
12
10
8
6
4
2
0
0.00
0.30
0.40
0.51
0.64
Diameter (mm)

(b)


Quantity (%)
12
10
8
6
4
2
0
0.00
0.32
0.40
0.51
0.62
0.75
Diameter (mm)

(c)



(e)

Figure 4.30 The effect of blowing agent loading on size distribution of HDPE/NR foam (a) 1.0 pphp, (b) 2.0 pphp, (c) 3.0 pphp, (d) 4.0 pphp, and (e) 5.0 pphp (series B)

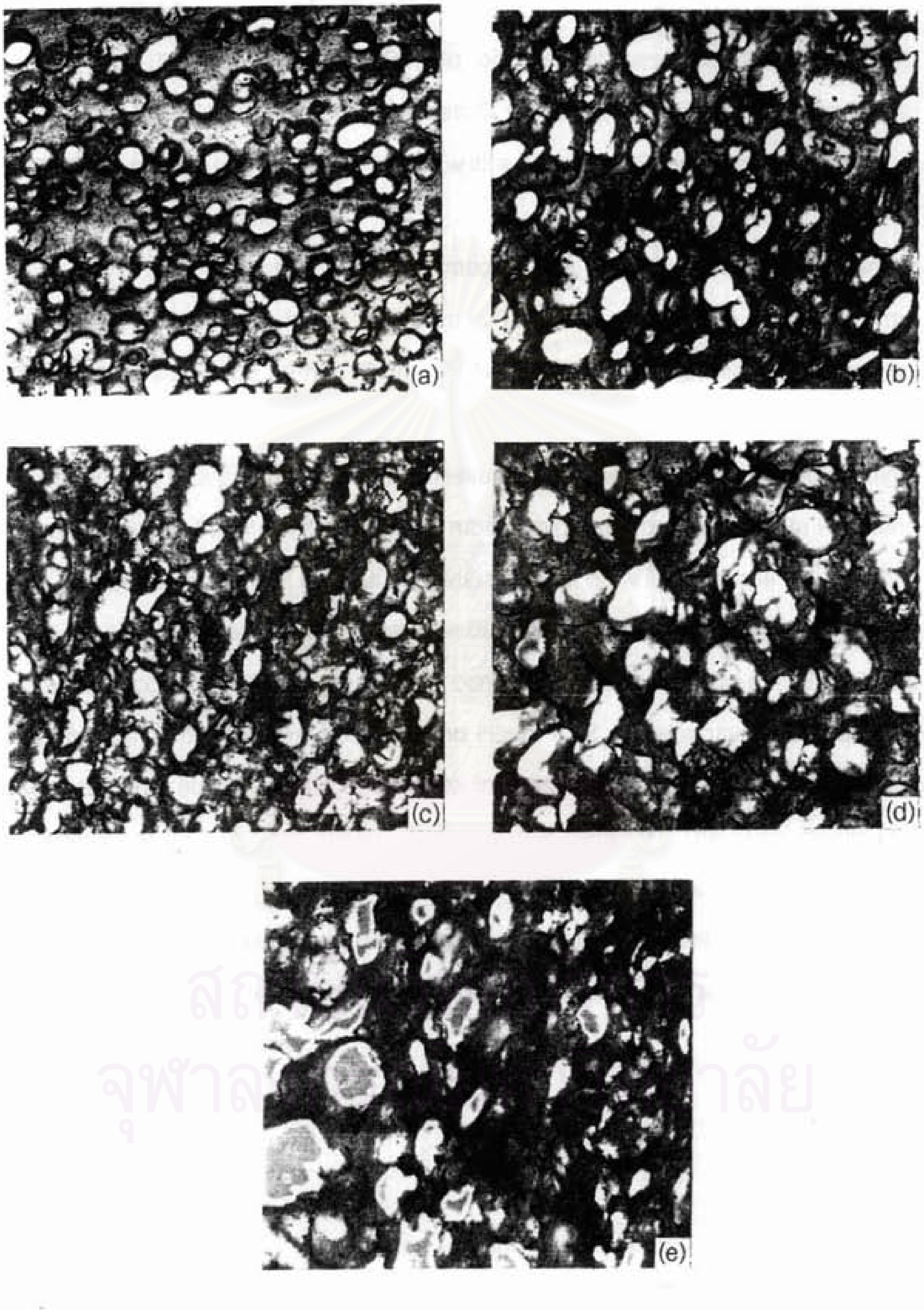


Figure 4.31 The effect of blowing agent loading on cell structures of HDPE/NR foam (a) 1.0 pphp, (b) 2.0 pphp, (c) 3.0 pphp, (d) 4.0 pphp, and (e) 5.0 pphp (series B)

4.4.3 Effect of HDPE/NR ratio

The effect HDPE/NR ratio on the cell structure and mechanical properties of HDPE/NR foams in series C was studied by varying the ratios of HDPE/NR blends from 90/10 to 50/50 (with a 10 pphp NR increment) in 2 pphp of the blowing agent loading.

The effects of HDPE/NR ratio on the cell structure and mechanical properties of HDPE/NR foams are given in Table 4.6 and Figures 4.32-4.40. From Figure 4.40 show that at the NR content higher than 20 pphp, the cell shape was distorted, and the average cell size, cell size distribution, maximum cell size, minimum cell size could not thereby measured. The distortion of the samples might occur because the strength of natural rubber might not be adequate to withstand the gas pressure. So that the gas bubbles could not grow in NR phase

The foam density increases but hardness, tensile strength and flexural strength decrease with increasing NR content, as show in Figures 4.32-4.34 and Figure 4.37. From Figures 4.35-4.36 and Figure 4.38, the elongation at break, tear strength and elastic modulus seem to increase with NR content and reach a maximum at 30 pphp NR content and decrease thereafter. The lower mechanical properties at high ratios of HDPE/NR blends are expected due to the degradation of natural rubber during the mixing process and non-crosslinking sites in natural rubber. The latter assumption can be improved by adding the suitable cross-linking agent in HDPE/NR blend.

Table 4.6 Effect of ratio HDPE/NR on the cell structure and mechanical properties of HDPE/NR foams.

Cell structure & mechanical properties	NR content (pphp)				
	10	20	30	40	50
Average cell size (mm)	0.34	0.40	-	-	-
Cell size distribution (mm)	0.08	0.09	-	-	-
Maximum cell size (mm)	0.51	0.70	-	-	-
Minimum cell size (mm)	0.15	0.21	-	-	-
Foam density (g/cm^3)	0.58	0.57	0.67	0.69	0.67
Hardness shore (A)	34±1	33±1	33±1	30±0	30±1
Tensile strength (MPa)	2.0±0.1	1.4±0.4	1.5±0.1	1.2±0.1	0.7±0.0
Elongation at break (%)	64±11	115±43	272±63	154±40	147±16
Tear strength (kN/m)	52.5±5	46.7±4	65.8±4	47.7±3	34±4
Flexural strength (MPa)	6.6±0.4	5.5±0.2	4.6±0.3	2.7±0.2	2.0±0.2
Elastic modulus (MPa)	218±23	155±19	263±25	148±45	104±63

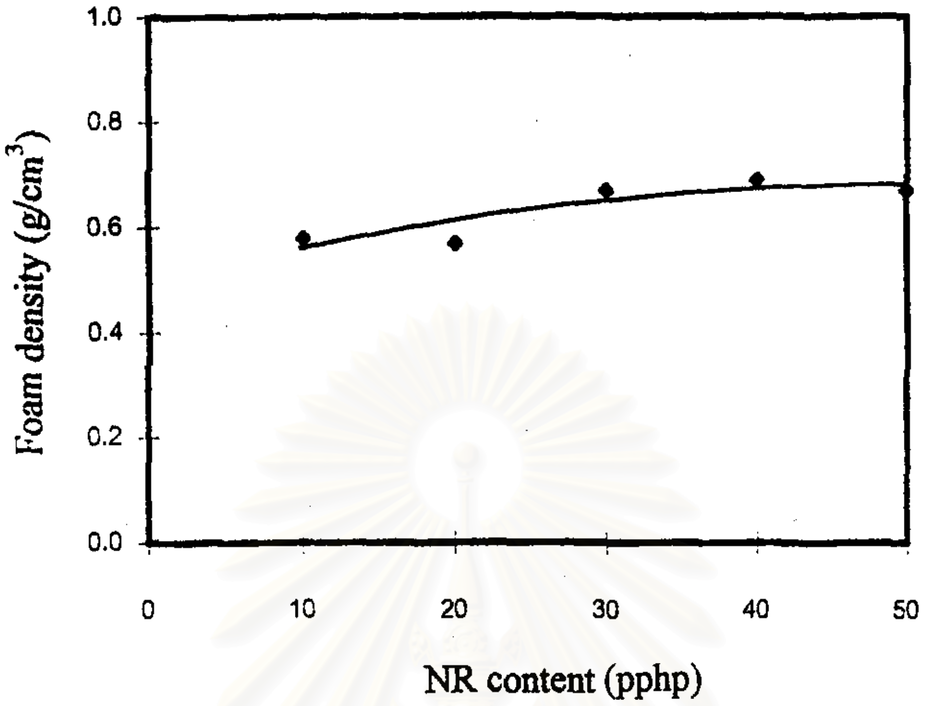


Figure 4.32 Effect of NR content on foam density

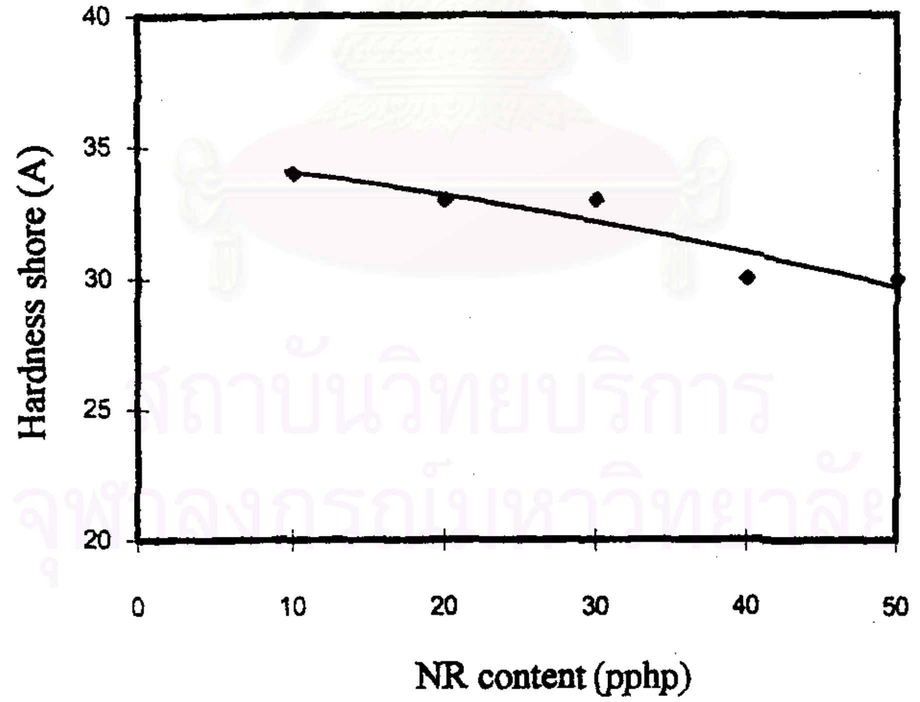


Figure 4.33 Effect of NR content on hardness

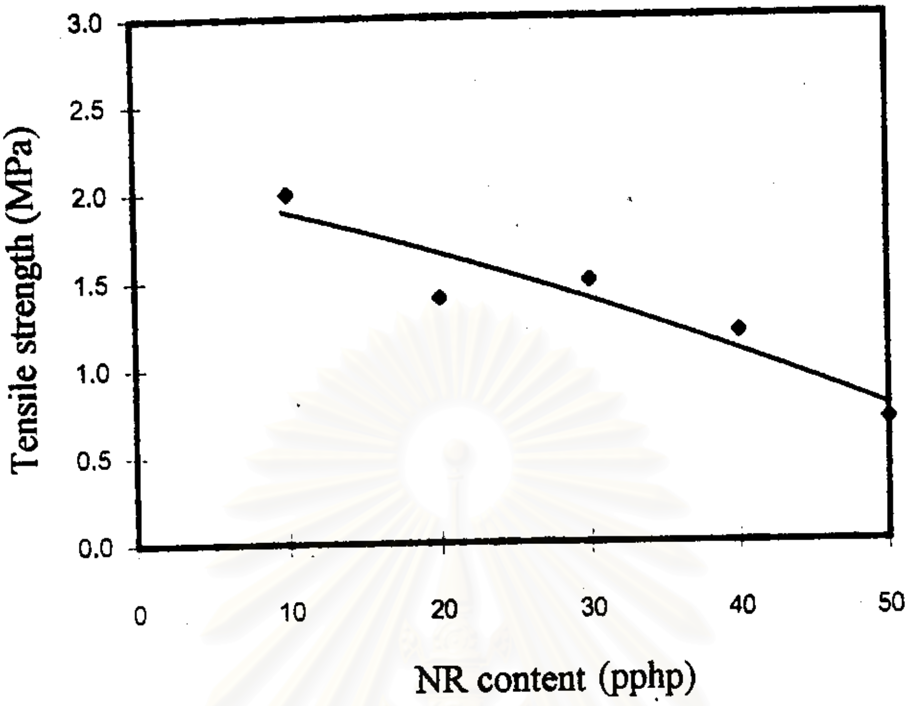


Figure 4.34 Effect of NR content on tensile strength

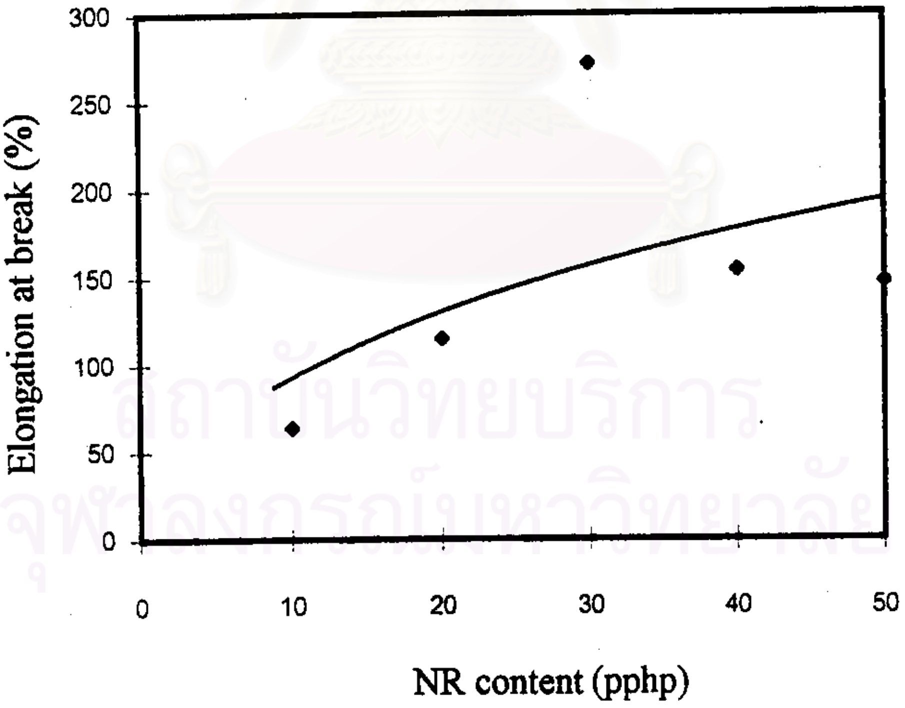


Figure 4.35 Effect of NR content on elongation at break

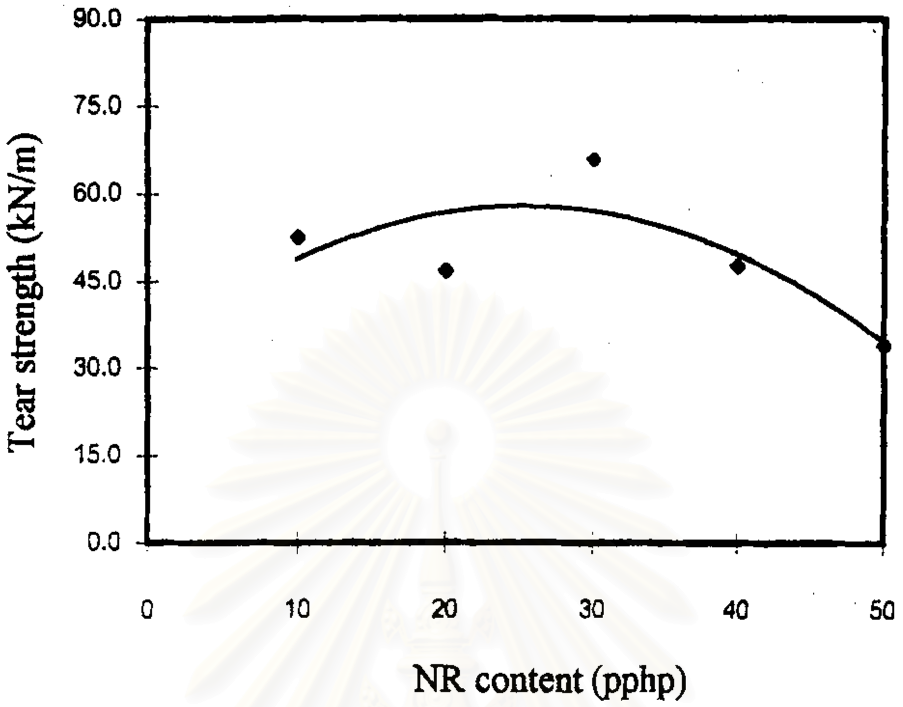


Figure 4.36 Effect of NR content on tear strength

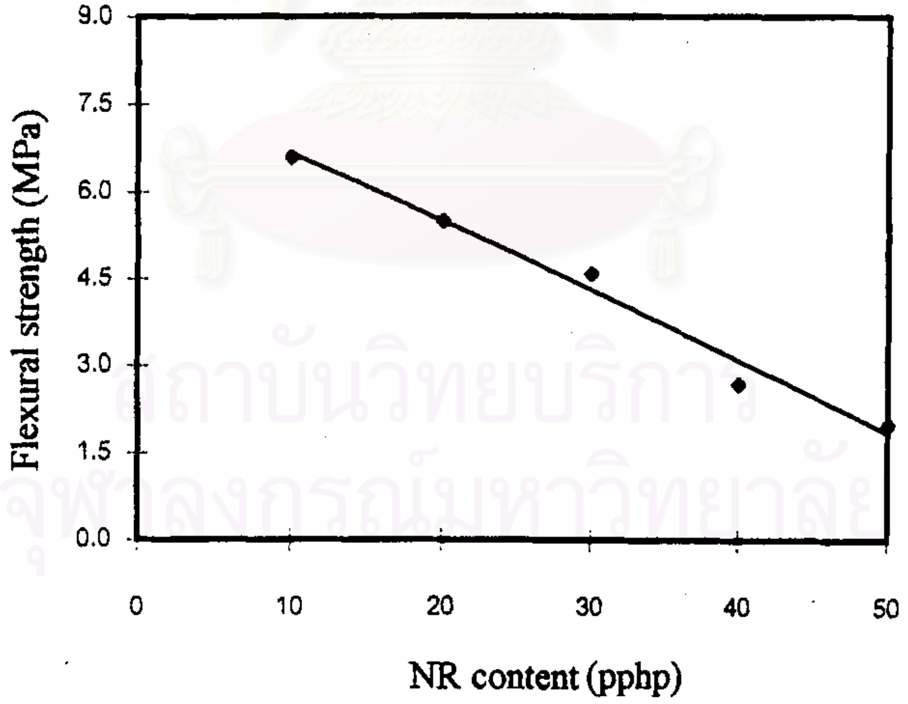


Figure 4.37 Effect of NR content on flexural strength

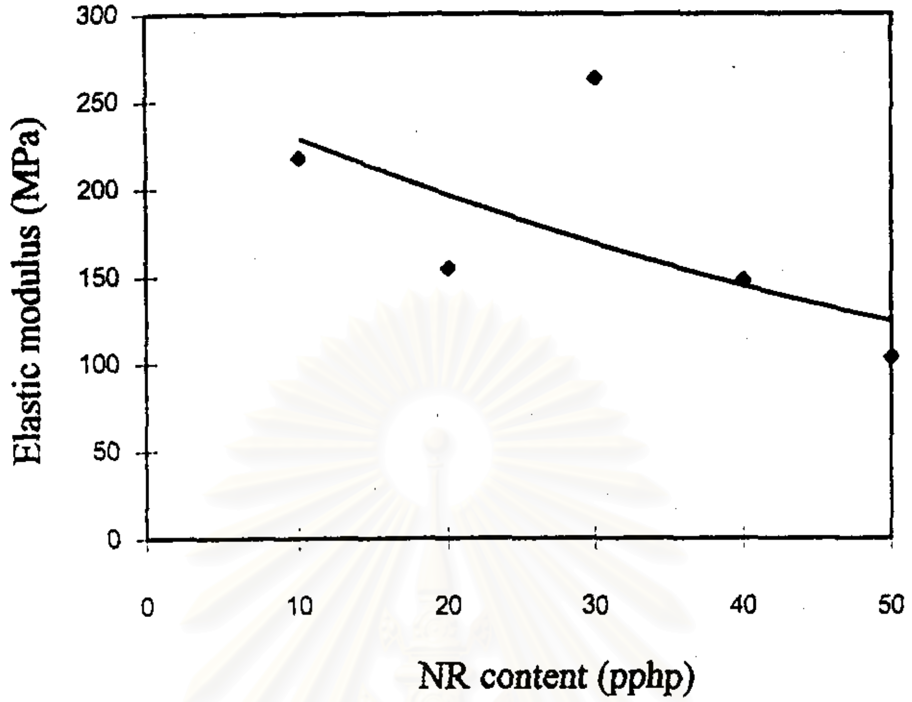


Figure 4.38 Effect of NR content on elastic modulus

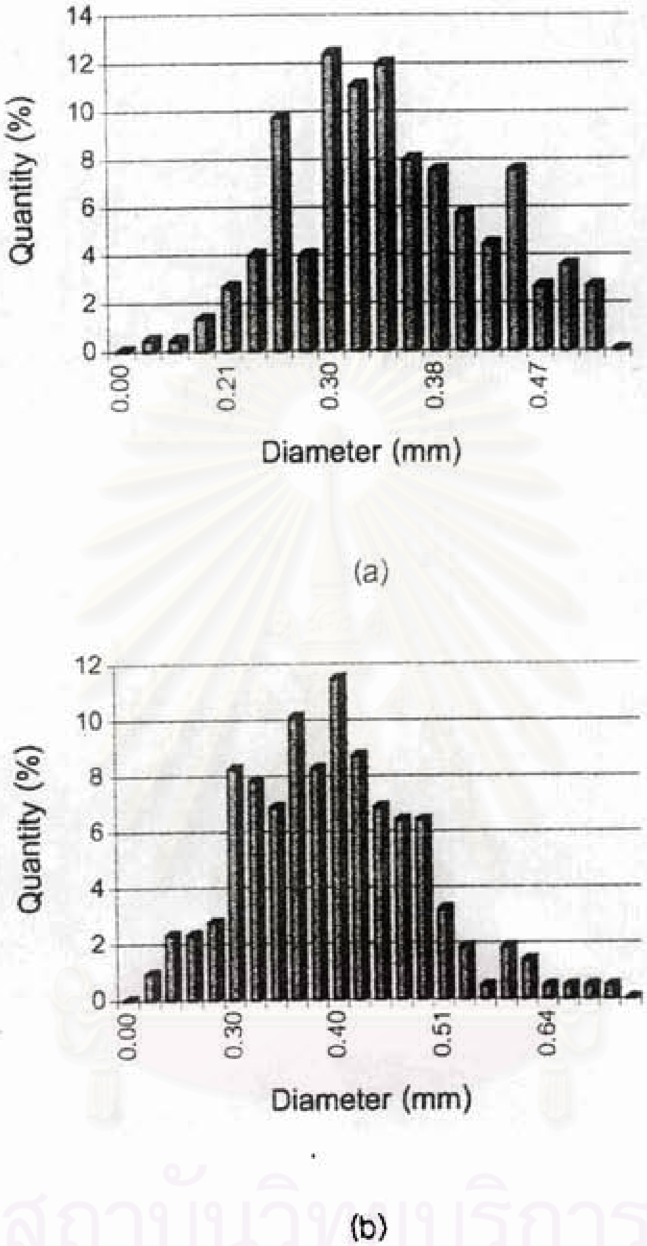


Figure 4.39 The effect of NR content on cell size distribution of HDPE/NR foam (a) 10 pphp, and (b) 20 pphp (series C)

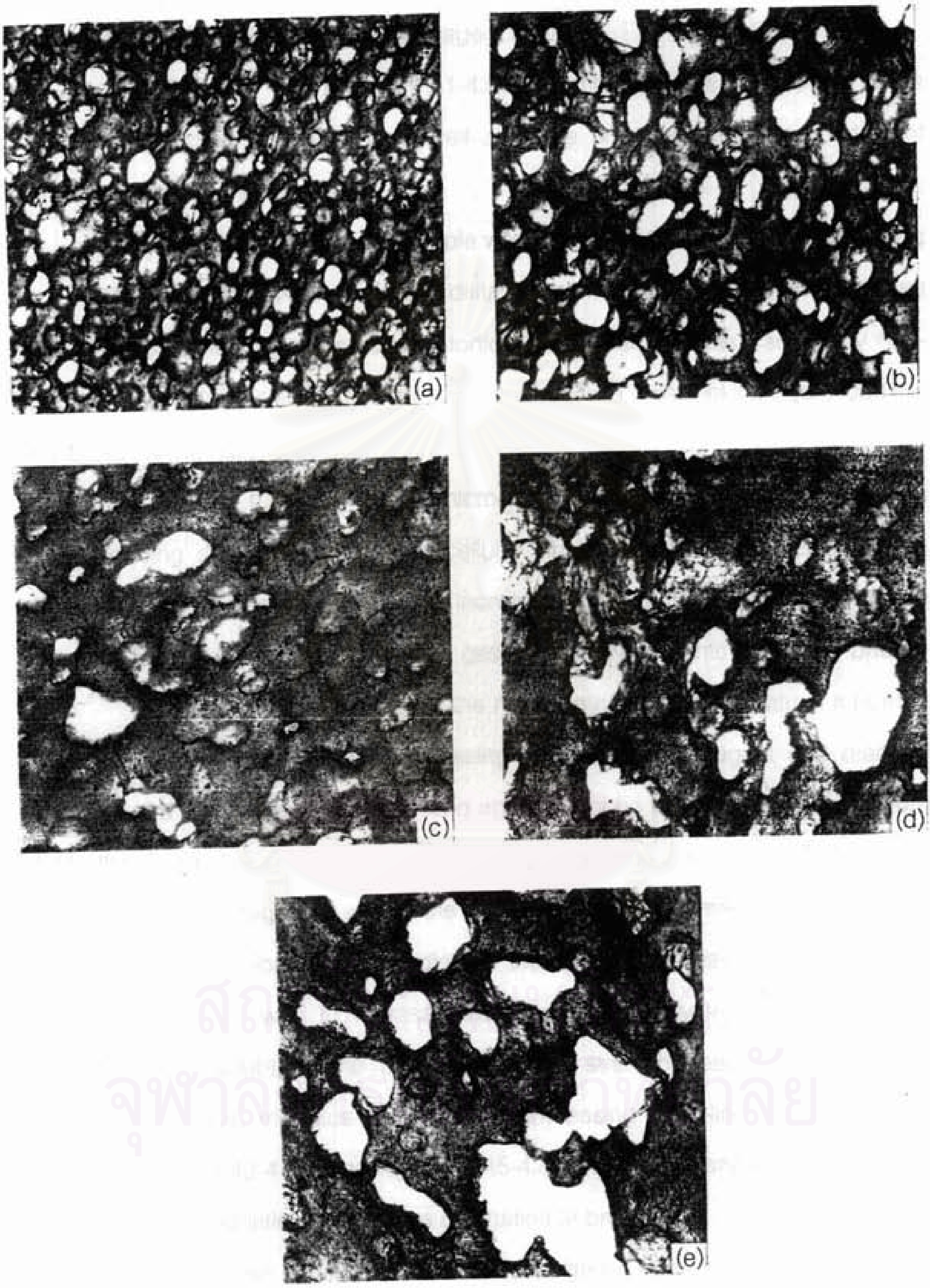


Figure 4.40 The effect of NR content on cell structures of HDPE/NR foam (a) 10 pphp, (b) 20 pphp, (c) 30 pphp, (d) 40 pphp, and (e) 50 pphp (series C)

4.4.4 Effect of the cross-linking agent loading

Table 4.7 and Figures 4.41-4.50 present the results of the effect of the cross-linking agent loading on the cell structure and mechanical properties of HDPE/NR foams of series D.

The cell shape of the sample was distorted at 0.2 pphp of cross-linking agent. Therefore, the average cell size distribution, maximum cell size and minimum cell size could not be measured. Distortion of this sample was caused by non-cross-linking behavior of the NR phase. Even too low a cross-linking agent loading, the cross-linking reaction could not occur.

Figure 4.50, the optical micrograph of 0.2 pphp of the cross-linking agent loading shows an elongated cellular structure with some interconnected cells. When the cross-linking agent is increased, the distribution of cells is widely dispersed which is anticipated as more gas bubbles evolved into the rubber phase.

The gel content, which is the measure of crosslink of natural rubber in HDPE/NR foam, increased with increasing the cross-linking agent and reached constant at a higher weight cross-linking agent 0.6 pphp (Figure 4.48). From Figure 4.41, the foam density increases with increasing cross-linking agent. Table 4.7 shows that the average cell size of the foam appears to be smaller with increasing cross-linking agent loading. According to the effect of increasing the amount of cross-linking agent was to increase the crosslink density which restricted the growth of gas bubbles. The hardness, tensile strength, tear strength, flexural strength and elastic modulus increased with increasing cross-linking agent loading , see in Figures 4.42-4.43, and Figures 4.45-4.47. Figure 4.44 shows that the cross-linking loading had little effect on the elongation at break.

Base on these results 0.6 pphp of cross-linking agent loading was used for further investigation because crosslink density did not in2creased at higher weight cross-linking agent 0.6 pphp.

Table 4.7 Effect of cross-linking agent loading on the cell structure and mechanical properties of HDPE/NR foams.

Cell structure & mechanical properties	Cross-linking agent loading (pphp)				
	0.2	0.4	0.6	0.8	1.0
Average cell size (mm)	-	0.56	0.48	0.47	0.50
Cell size distribution (mm)	-	0.12	0.12	0.11	0.10
Maximum cell size (mm)	-	0.85	0.98	0.98	0.77
Minimum cell size (mm)	-	0.28	0.23	0.21	0.28
Foam density (g/cm^3)	0.42	0.46	0.54	0.59	0.64
Gel content (%)	99.2	99.3	99.6	99.6	99.6
Hardness shore (A)	35±1	35±1	37±1	36±1	36±1
Tensile strength (MPa)	0.7±0.0	0.9±0.1	2.0±0.1	1.2±0.0	1.3±0.1
Elongation at break (%)	136±25	183±28	74±4	182±23	127±25
Tear strength (kN/m)	25.8±1	47.0±3	32.5±2	44.2±6	44.4±4
Flexural strength (MPa)	2.3±0.3	2.6±0.2	4.0±0.1	4.0±0.3	3.5±0.1
Elastic modulus (MPa)	48±10	64±5	144±9	178±38	143±10

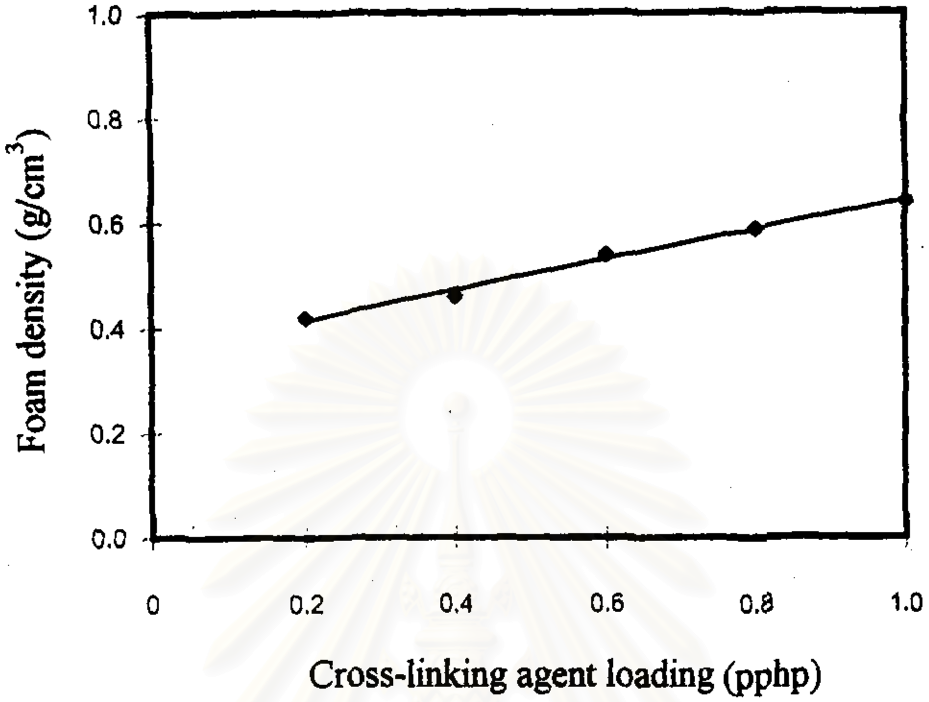


Figure 4.41 Effect of cross-linking agent loading on foam density

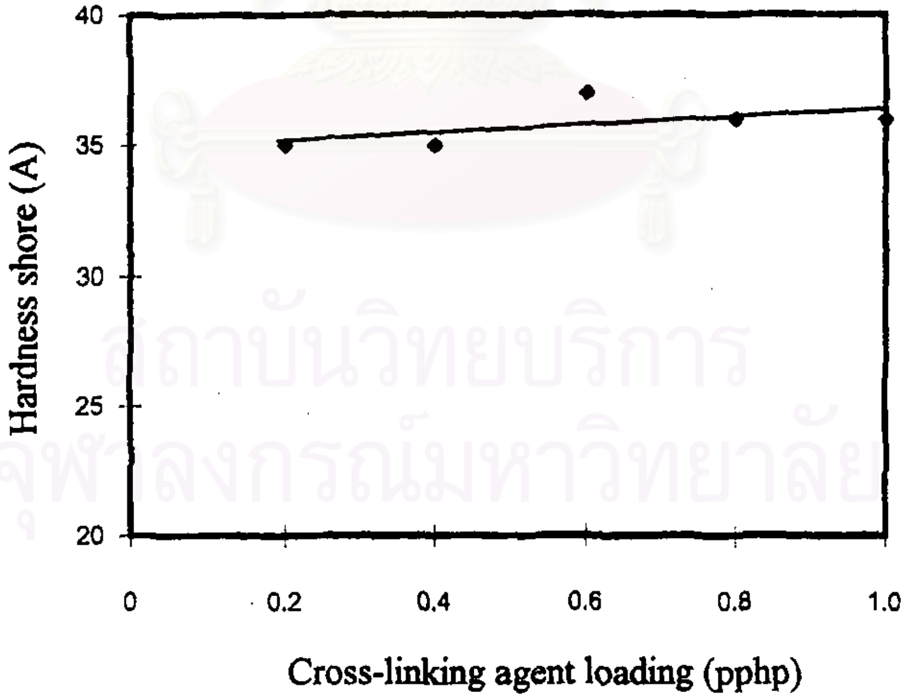


Figure 4.42 Effect of cross-linking agent loading on hardness

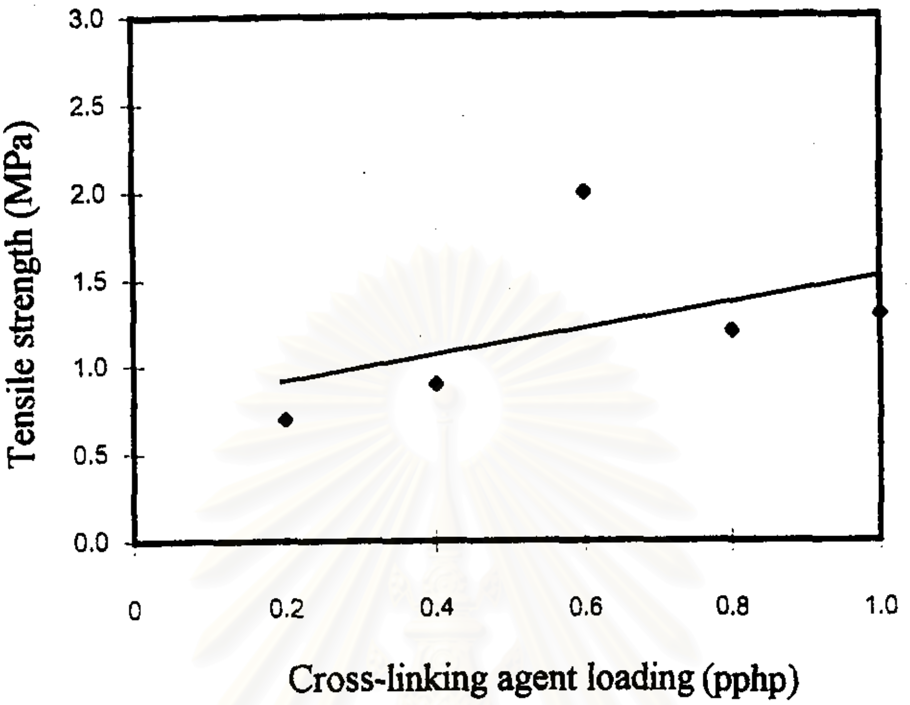


Figure 4.43 Effect of cross-linking agent loading on tensile strength

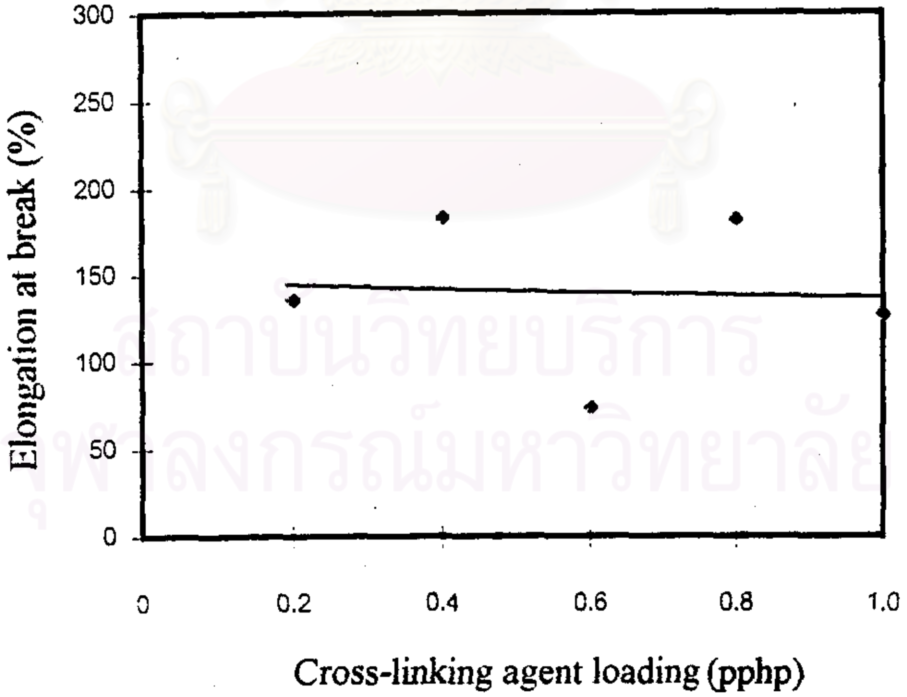


Figure 4.44 Effect of cross-linking agent loading on elongation at break

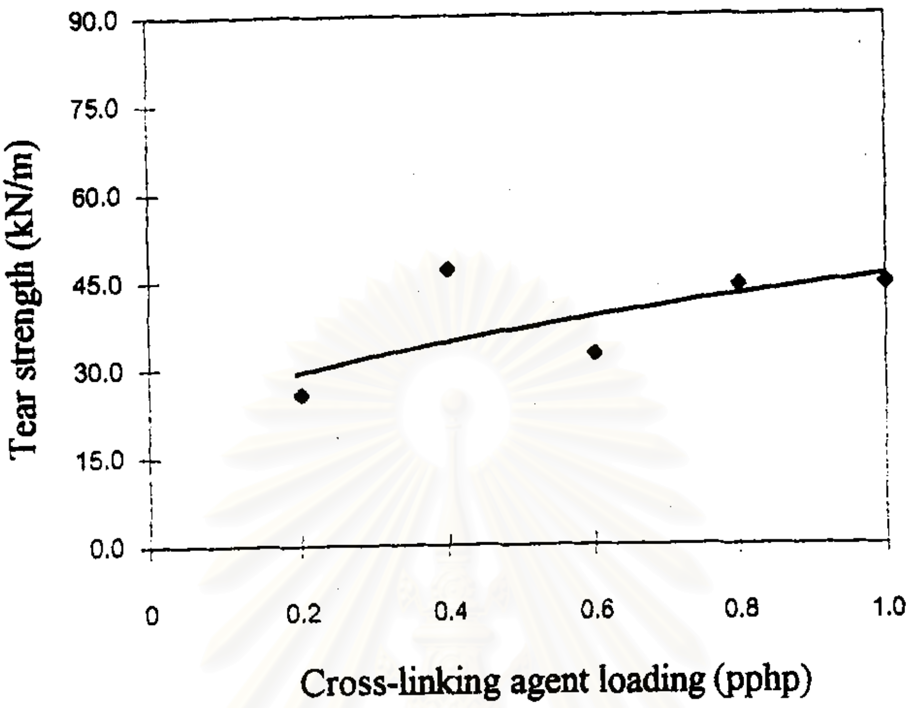


Figure 4.45 Effect of cross-linking agent loading on tear strength

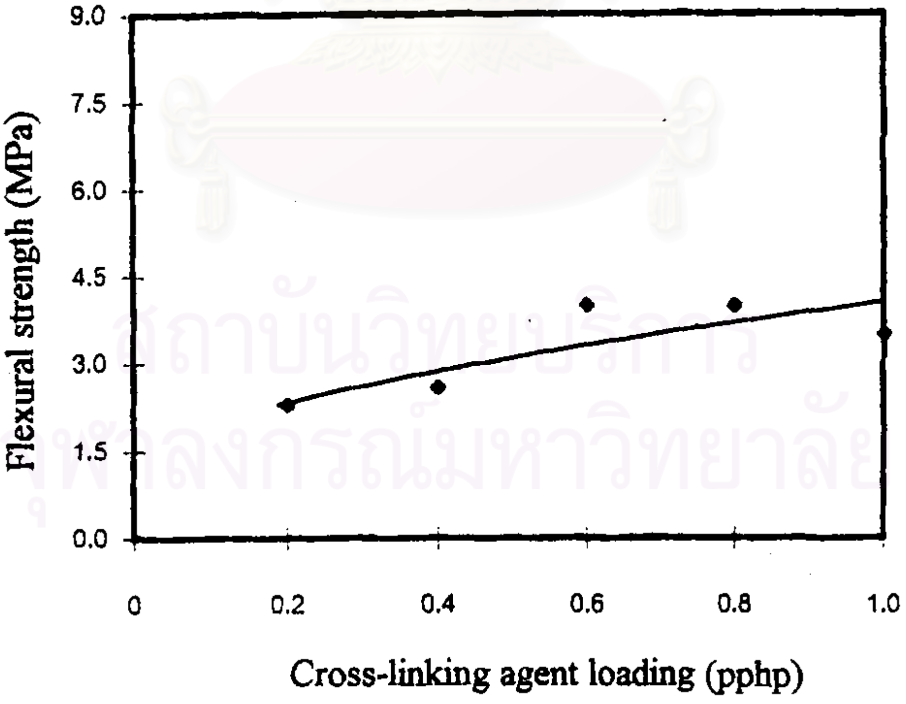


Figure 4.46 Effect of cross-linking agent loading on flexural strength

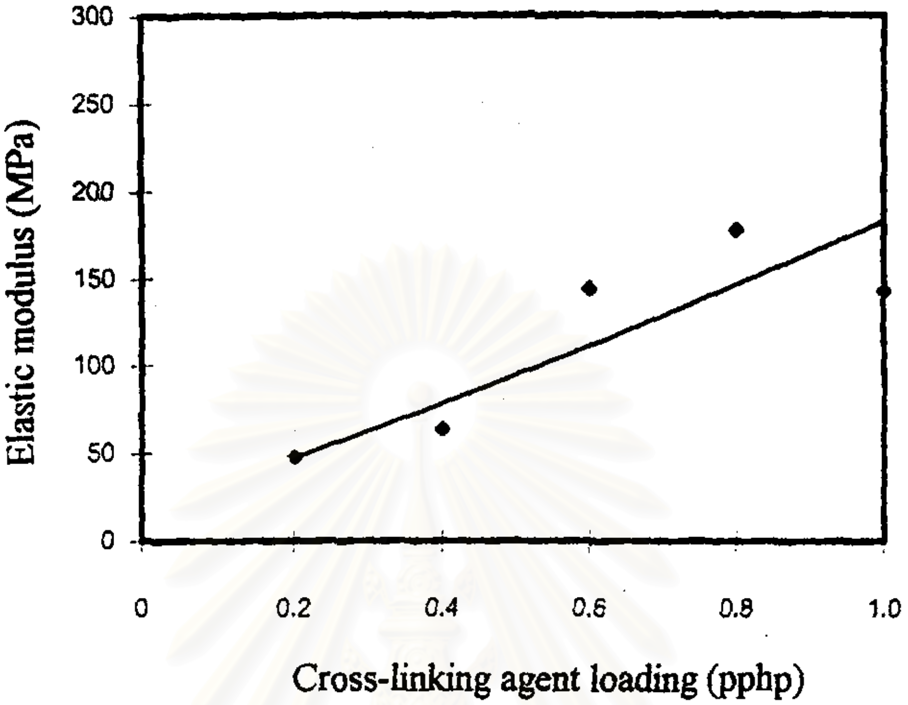


Figure 4.47 Effect of cross-linking agent loading on elastic modulus

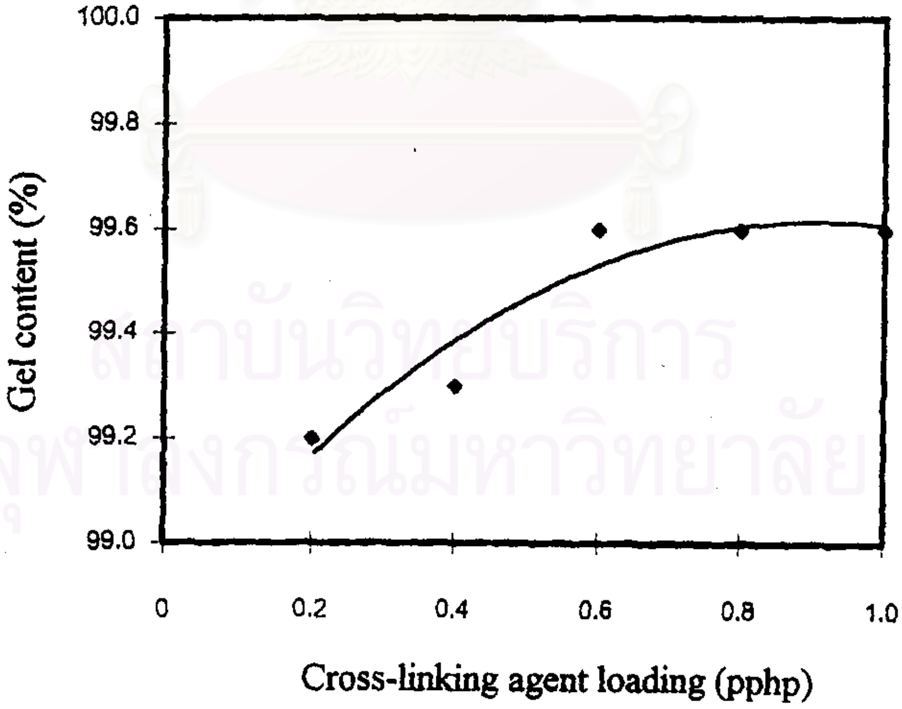
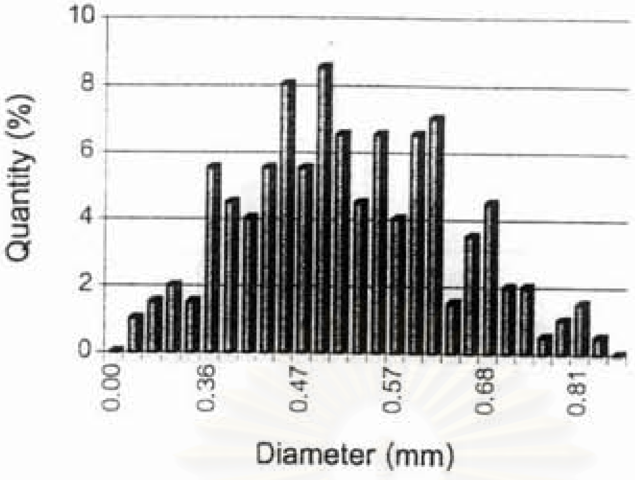
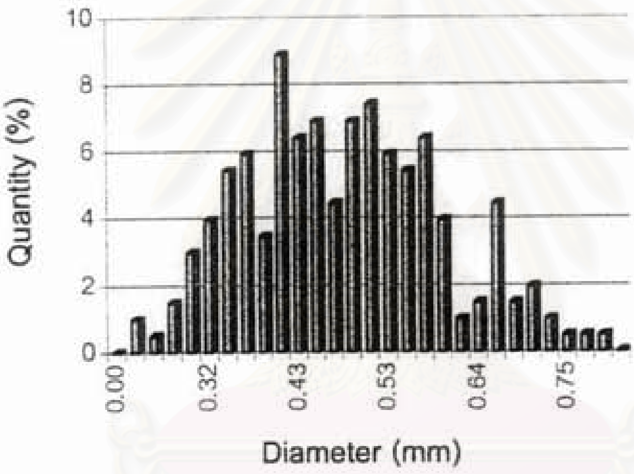


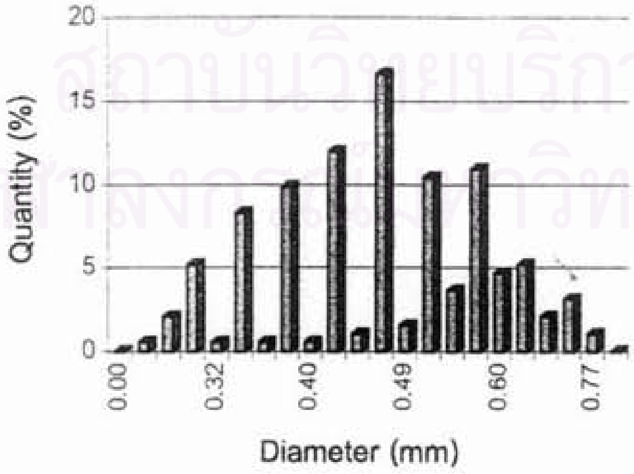
Figure 4.48 Effect of cross-linking agent loading on gel content


10
8
6
4
2
0
Quantity (%)
0.00
0.36
0.47
0.57
0.68
0.81
Diameter (mm)

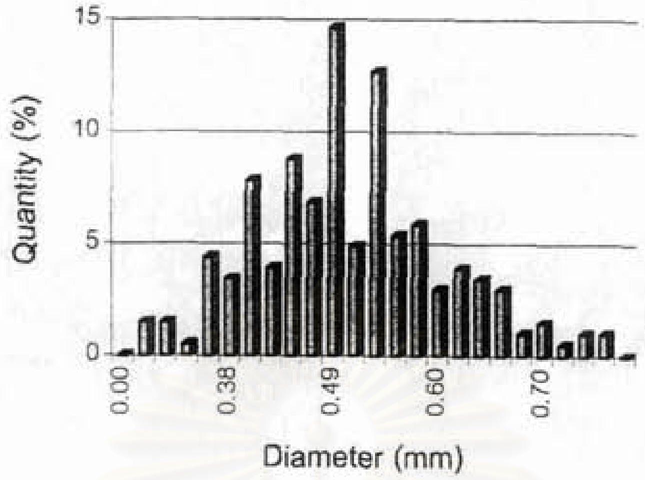
(a)


10
8
6
4
2
0
Quantity (%)
0.00
0.32
0.43
0.53
0.64
0.75
Diameter (mm)

(b)


20
15
10
5
0
Quantity (%)
0.00
0.32
0.40
0.49
0.60
0.77
Diameter (mm)

(c)



(d)

Figure 4.49 The effect of cross-linking agent loading on cell size distribution of HDPE/NR foam (a) 0.4 pphp, (b) 0.6 pphp, (c) 0.8 pphp, and (d) 1.0 pphp (series D)

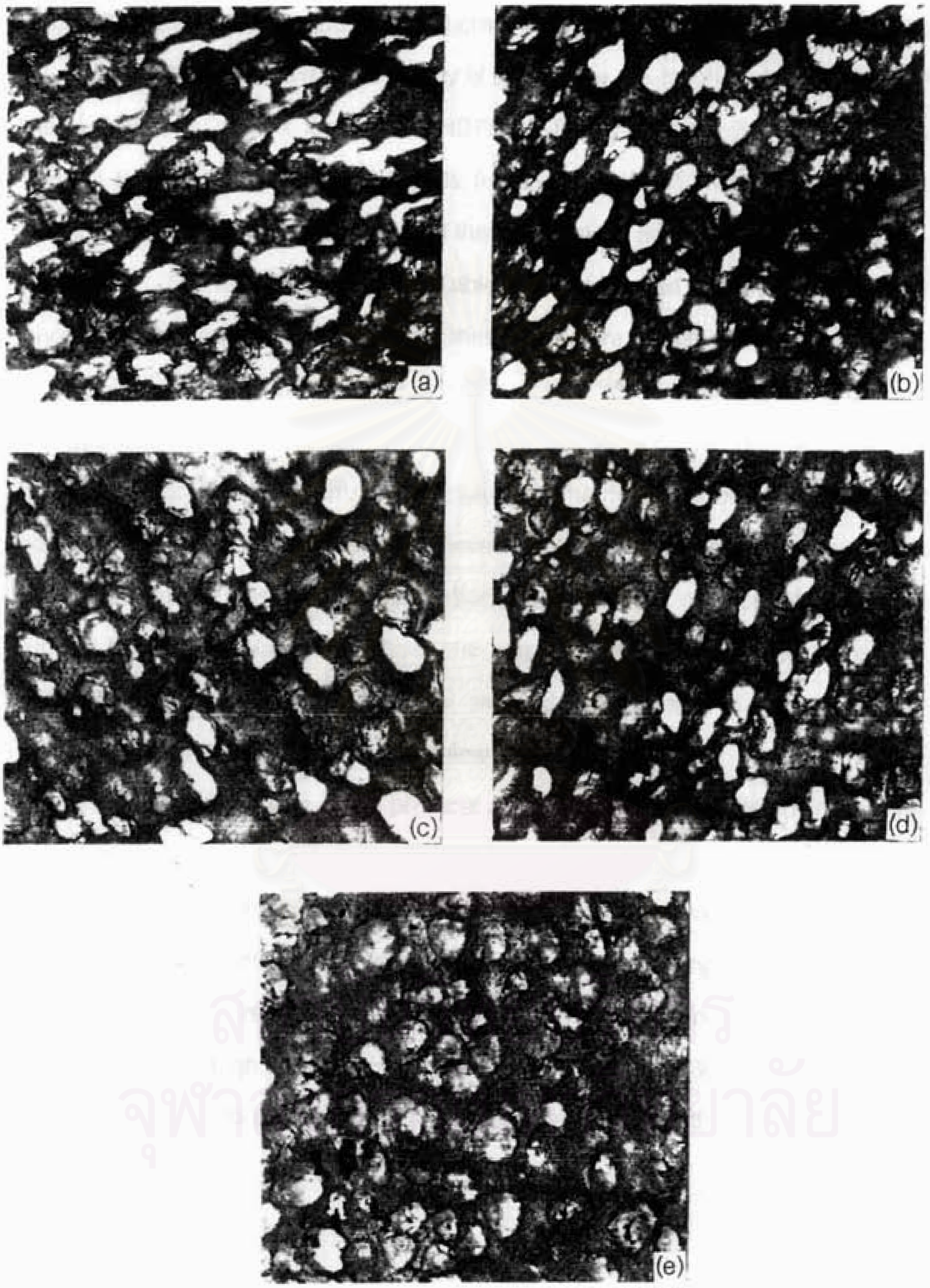


Figure 4.50 The effect of cross-linking agent loading on cell structures of HDPE/NR foam (a) 0.2 pphp, (b) 0.4 pphp, (c) 0.6 pphp, (d) 0.8 pphp, and (e) 1.0 pphp (series D)

4.4.5 Effect of HDPE/NR ratio at a fixed cross-linking agent loading

The objective of this study is to improve the mechanical properties of the high-ratio HDPE/NR foams. The HDPE/NR foams of series E was studied by varying the ratios of HDPE/NR blends from 90/10 to 50/50 with 2 pphp of the blowing agent loading and 0.6 pphp of the cross-linking agent loading.

The results are given in Table 4.8 and Figures 4.51-4.59. The optical photographs showing the structures of these foams are displayed in Figure 4.60.

From Figure 4.60, the added crosslink agent facilitates the growth of the gas bubbles in 30 pphp NR blend, while the 40 pphp NR and 50 pphp NR blends did not produce foams in the polymeric matrix. The average cell size, cell size distribution, maximum cell size, minimum cell size were then not available. It might be that the gas was released after the crosslinking reaction of the natural rubber had taken place. Therefore, the gas bubbles were trapped within the network which were unable to grow since the crosslinked rubber could not permanently be deformed or could not flow.

A comparison of the physical properties of the HDPE/NR blends at the same ratio without cross-linking agent and with cross-linking agent is shown in Table 4.9 for all the HDPE/NR ratios. It is concluded that the cross-linking agent can improve hardness and tensile strength but decreases the elongation at break, tear strength, flexural strength and elastic modulus of the blend. The mechanical properties of the high ratios of HDPE/NR blends (more than 30 pphp NR content) were still poor due to the degradation of natural rubber during the mixing process.

Table 4.8 Effect of HDPE/NR ratio at a fixed cross-linking agent loading on the cell structure and mechanical properties of HDPE/NR foams.

Cell structure & *mechanical* properties	Varying NR content at fixed cross-linking agent loading				
	10	20	30	40	50
Average cell size (mm)	0.34	0.43	0.48	-	-
Cell size distribution (mm)	0.06	0.11	0.12	-	-
Maximum cell size (mm)	0.51	0.77	0.98	-	-
Minimum cell size (mm)	0.21	0.21	0.23	-	-
Foam density (g/cm^3)	0.65	0.58	0.54	0.62	0.82
Gel content (%)	99.2	99.3	99.6	99.5	99.6
Hardness shore (A)	36±1	35±1	37±1	34±1	33±1
Tensile strength (MPa)	2.3±0.2	1.6±0.1	2.0±0.1	0.8±0.1	0.8±0.1
Elongation at break (%)	61±19	122±52	74±4	109±43	48±16
Tear strength (kN/m)	60.4+4	51.9+4	32.5+2	33.7+4	36.9+2
Flexural strength (MPa)	7.3±0.2	4.5±0.6	4.0±0.1	1.7±0.1	1.7±0.2
Elastic modulus (MPa)	332±20	146±36	144±9	56±13	47±19

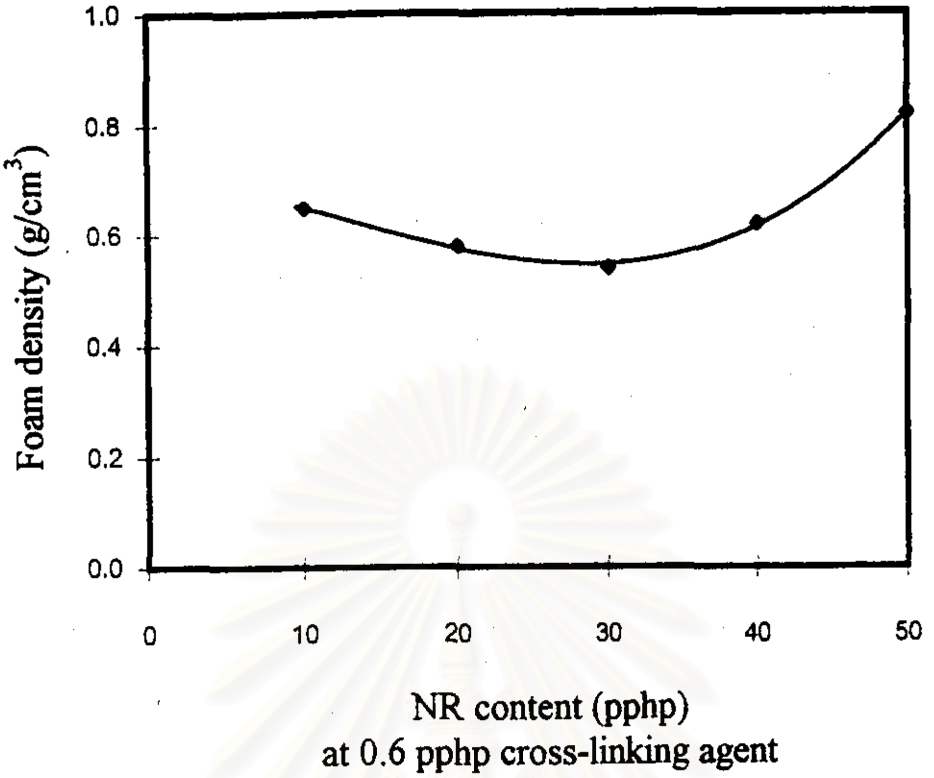


Figure 4.51 Effect of NR content at fixed cross-linking agent loading on foam density

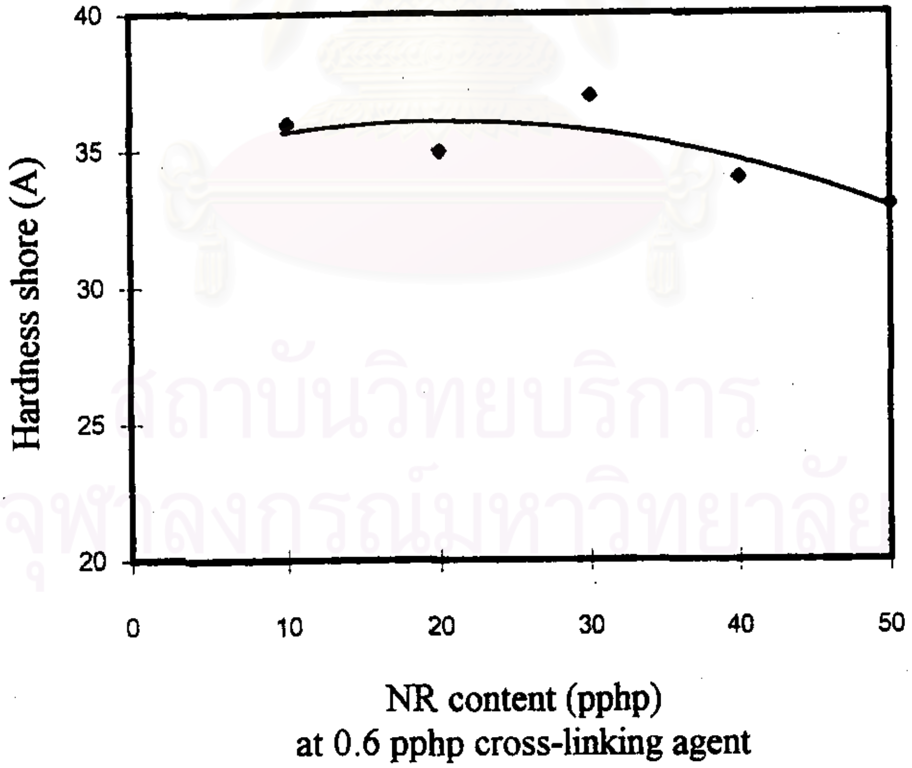


Figure 4.52 Effect of NR content at fixed cross-linking agent loading on hardness

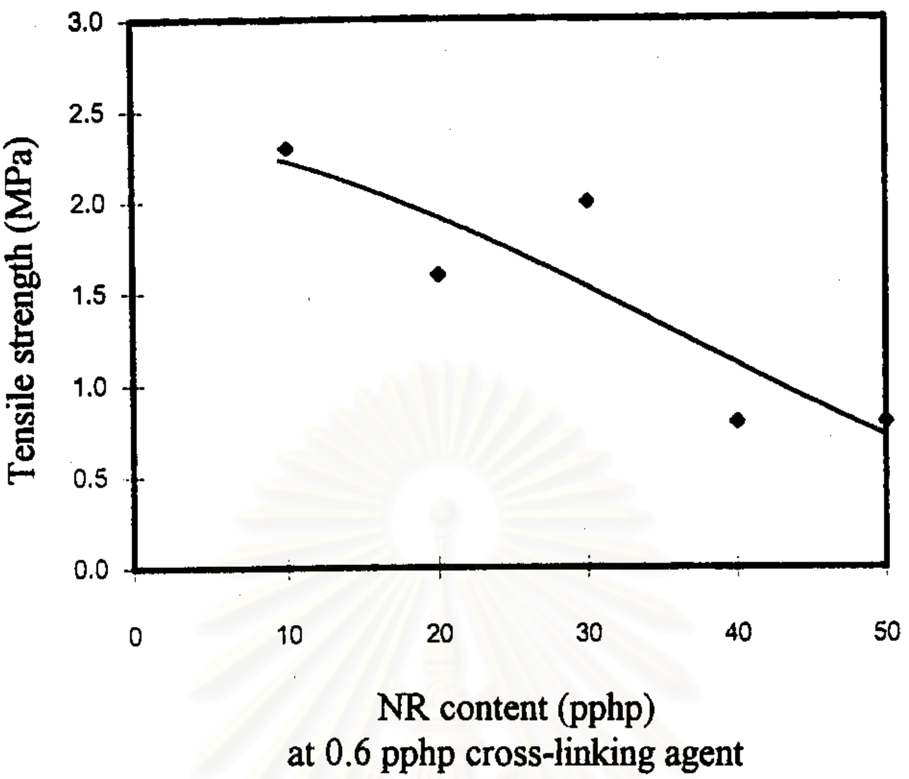


Figure 4.53 Effect of NR content at fixed cross-linking agent loading on tensile strength

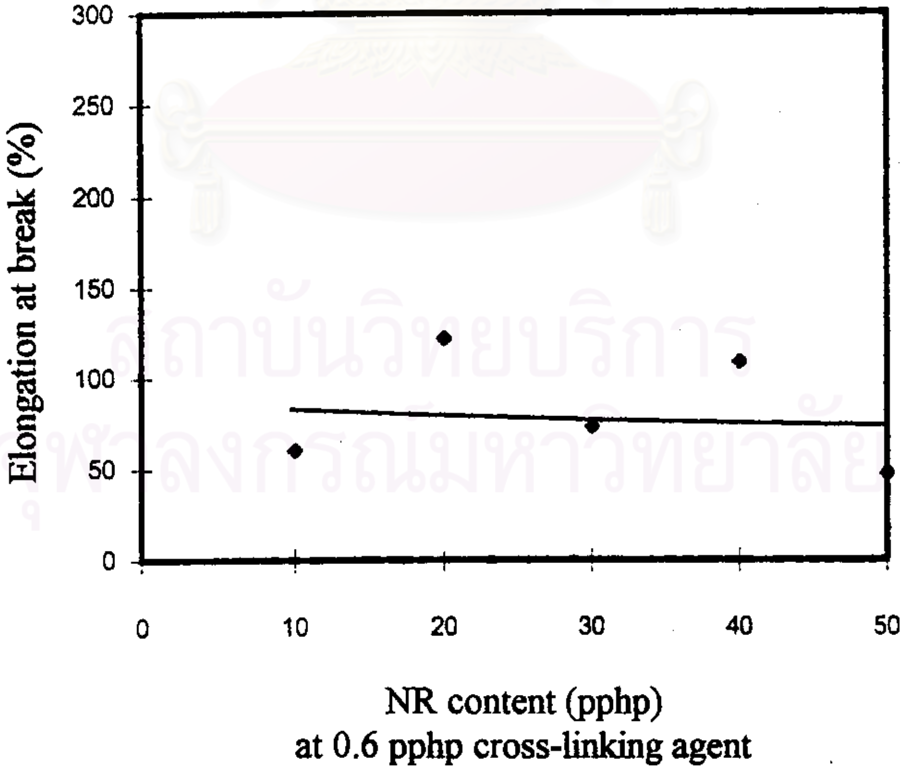


Figure 4.54 Effect of NR content at fixed cross-linking agent loading on elongation at break

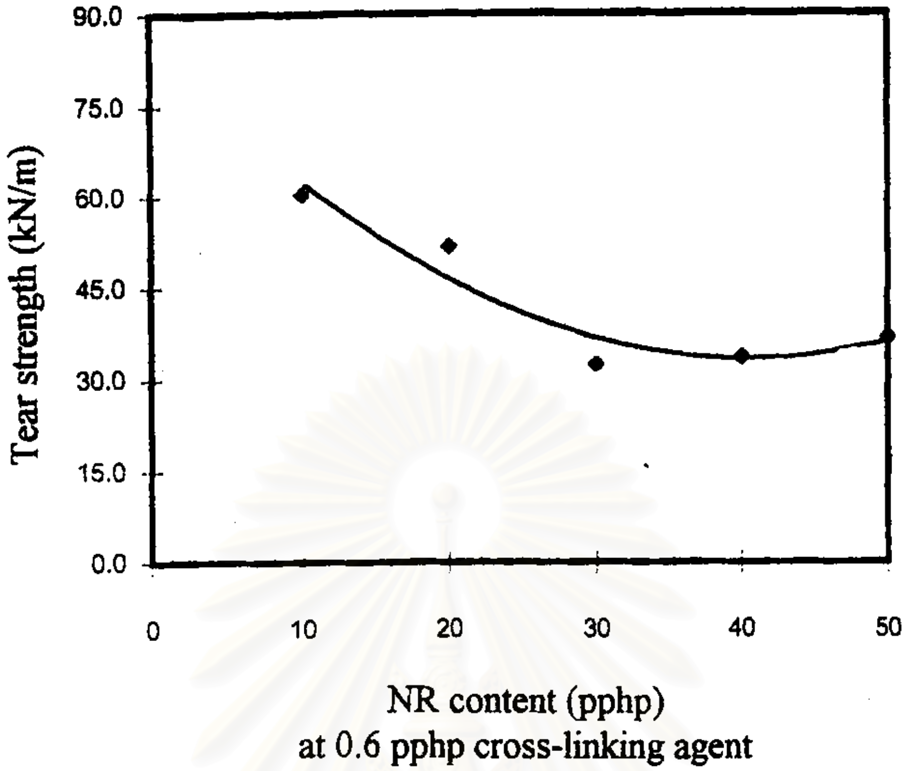


Figure 4.55 Effect of NR content at fixed cross-linking agent loading on tear strength

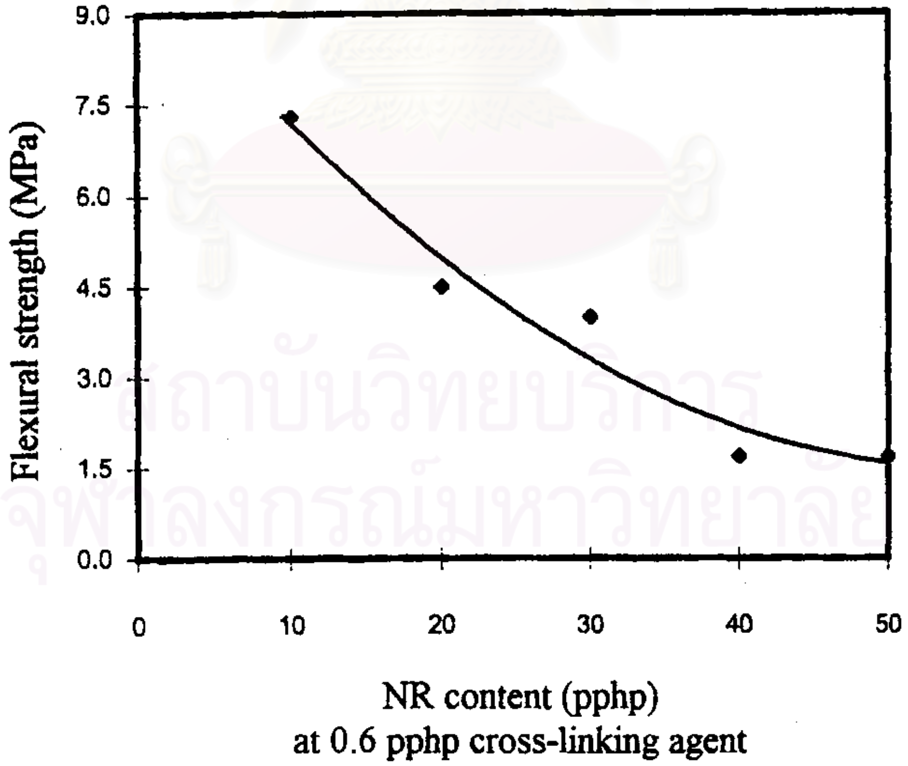


Figure 4.56 Effect of NR content at fixed cross-linking agent loading on flexural strength

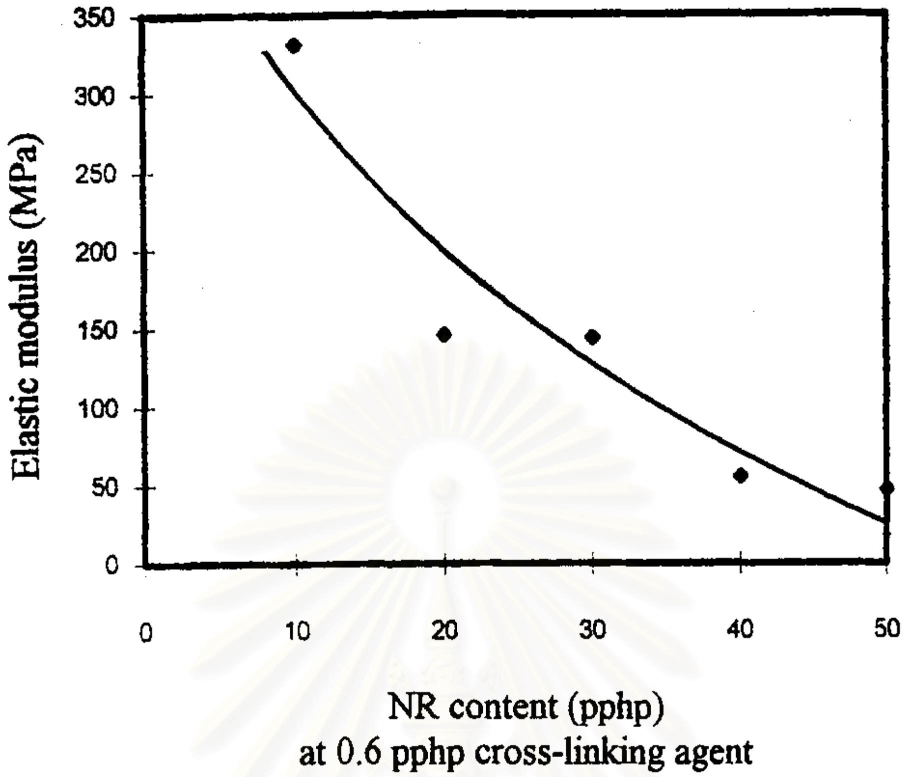


Figure 4.57 Effect of NR content at fixed cross-linking agent loading on elastic modulus

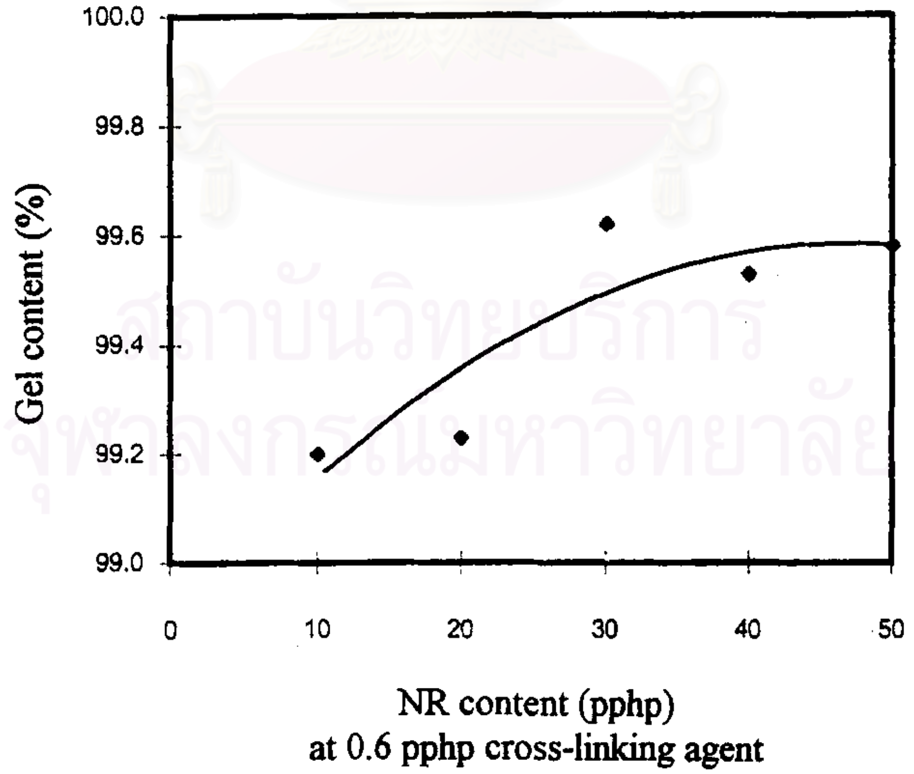


Figure 4.58 Effect of NR content at fixed cross-linking agent loading on gel content

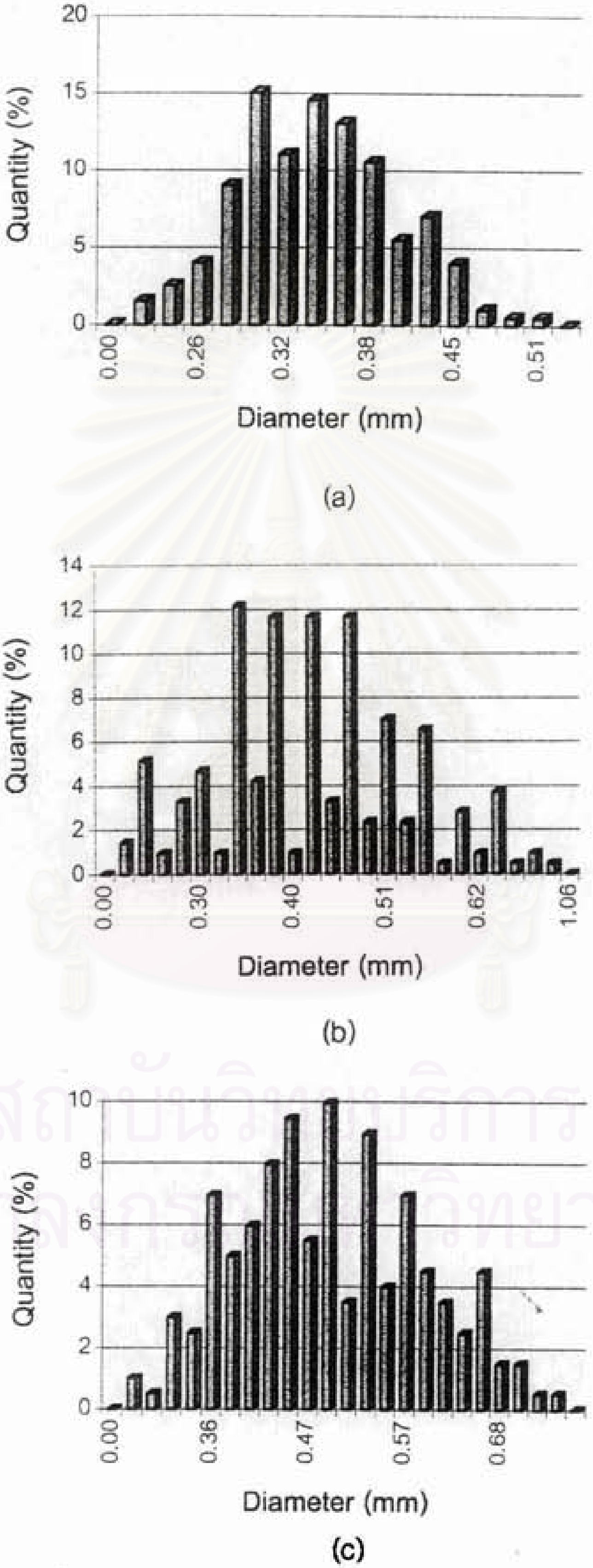


Figure 4.59 The effect of NR content at 0.6 pphp cross-linking agent on cell size distribution of HDPE/NR foam (a) 10 pphp,(b) 20 pphp, and (c) 30 pphp (series E)

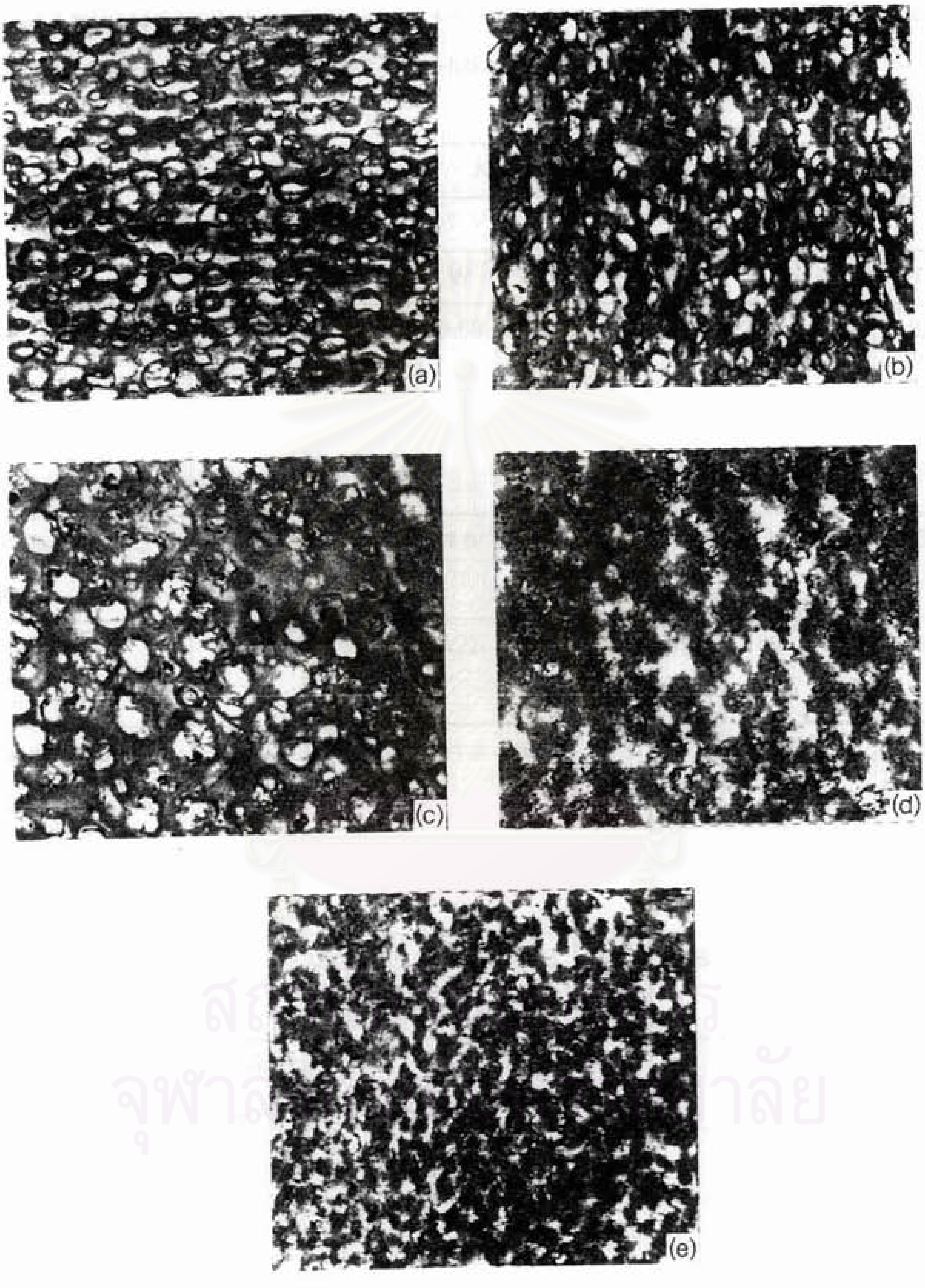


Figure 4.60 The effect of NR content at 0.6 pphp cross-linking agent on cell structures of HDPE/NR foam (a) 10 pphp, (b) 20 pphp, (c) 30 pphp, (d) 40 pphp, and (e) 50 pphp (series E)

Table 4.9 Comparison of the mechanical properties at the same ratio of HDPE/NR blends without cross-linking agent and with cross-linking agent

Properties	NR content (pphp)									
	10		20		30		40		50	
	WO	W	WO	W	WO	W	WO	W	WO	W
Foam density, (g/cm^3)	0.58	0.65	0.57	0.58	0.67	0.52	0.69	0.62	0.67	0.82
Hardness shore (A)	34	36	33	35	33	37	30	34	30	33
Tensile strength, (MPa)	2.0	2.3	1.4	1.6	1.5	2.0	1.2	0.8	0.7	0.8
Elongation at break, (%)	64	61	115	122	272	74	154	109	147	48
Tear strength, (kN/m)	52.5	60.4	46.7	51.9	65.8	32.5	47.7	33.7	34	36.9
Flexural modulus, (MPa)	6.6	7.3	5.5	4.5	4.6	4.0	2.7	1.7	2.0	1.7
Elastic modulus, (MPa)	218	332	155	146	263	144	148	56	104	47

WO Without the cross-linking agent

W With the cross-linking agent

4.5 Comparison of the mechanical properties of HDPE/NR foam with other material of foam.

To envisage possible applications of HDPE/NR foam, a comparison of some properties with other materials is discussed.

High-density polyolefin foams in the density range of 10-40 lb/ft^3 (160-641 kg/m^3) are rapidly moving into many areas previously occupied by products of solid polymers or natural cellular materials such as cork or wood. For example, the extrusion-injection-molded structural foams are being used as fan shrouds, tote boxes, quality furniture, and warehouse pallets. Also, corks, fishing lures, tools, paintbrush handles, toys, etc. can all be functionally and economically replaced by structural foam moldings of high-density polyolefin foams. High density cellular polyethylene has been used as primary insulation for communication cable for several years. Its good electrical properties permit the space between conductors to be reduced without increasing the impedance[31].

The modification of high-density polyethylene foam materials by adding natural rubber serves for the purpose of transferring to the foam material, the physical properties such as improved mechanical resistance, higher elasticity, and higher flexibility. Furthermore, natural rubber is less expensive as compared with high-density polyethylene and its use will increase consumption of natural rubber in the country. A comparison some properties of HDPE/NR foam with other materials is shown in Table 4.10.

Plastic foam can be classified into 3 groups as follows[8] :

1. A rigid plastic which has a stiffness or apparent modulus of elasticity, E, greater than 7,000 kg/cm^2 (100,000 psi) at 23 °C,
2. A semirigid plastic which has a value of E between 700 kg/cm^2(10,000 psi) and 7,000 kg/cm^2 (100,000 psi),

Table 4.10 Comparison of some mechanical properties of HDPE/NR with other materials

Properties	HDPE/NR foam			PE/IB[a] foam[16]	HDPE	Expanded	Expanded	Latex foam	PVC closes
	90/10	80/20	70/30	70/30	foam[16]	NR, type A[8]	NR, type B[8]	type A[8]	cell type A[8]
Density, kg/m^3	650	580	520	400	130	56	320	80	56
Indentation load deflection, kg	–	–	–	–	–	–	–	8	34
Tensile strength, kg/cm^2	23.5	16.3	20.4	50.7	26.0	0.35	2.1	1.05	–
Tensile elongation, %	61	122	74	236	305	–	–	310	
Compression set, %	–	–	–	–	–	–	–	10	15
Rebound resilience, %	–	–	–	–	–	–	–	73	
Tear strength, kg/cm	60.4	51.9	32.5	–	–	–	–	–	–
Flexural strength, kg/cm^2	74.5	46.0	40.8	–	–	–	–	–	–
Elastic modulus, kg/cm^2	3386	1489	1469	–	–	–	–	–	–

a Expanded polyisobutylene modified linear polyethylene foams

3. A nonrigid plastic or a flexible cellular plastic which has a value of E of less than 700 kg/cm^2(10,000 psi).

The modulus of elasticity of HDPE/NR foam has value between 3,386 kg/cm^2 and 479 kg/cm^2. The HDPE/NR foam exhibit properties between semirigid and flexible plastic foam that depend on foaming process variables and the cell structure of HDPE/NR foam is closed cell. The suggested applications of HDPE/NR foam are shown in table 4.11.

Table 4.11 Types of cellular polymer and their principal application[15].

	Flexible		Rigid	
Cell structure	Closed cell	Open cell	Closed cell	Open cell
Principal application	● Thermal insulation ● Buoyancy ● Packaging ● Gaskets	● Acoustic insulation ● Cushioning ● Filtration ● Packaging	● Thermal insulation ● Buoyancy ● Construction	● Acoustic insulation ● Filtration

To summarize, density, cell structure, blowing agent composition, and resin structure are important parameters that determine performance in foams. These parameters are regulate to design composites tailor-made foams.