CHAPTER IV

RESULTS AND DISCUSSION

The graft copolymers of MMA and ST onto EPDM rubber were prepared by solution polymerization using benzoyl peroxide as an initiator. The conversion, grafting efficiency, percentage of free rubber, percentage of copolymer and percentage of graft copolymer were recorded as functions of reaction temperature, rubber concentration and reaction time. The structure of graft product was also characterized by FT-IR and ^{1}H-NMR spectroscopy. The gross graft EPDM (GEPDM) was added into the MMA-ST syrup during the stage of bulk polymerization for preparing the acrylic sheet by casting process. The mechanical properties, optical properties and morphology of the modified acrylic sheets were investigated. The retention of mechanical properties after thermal and ultraviolet (UV) aging including the kinetics of thermal degradation of the acrylic sheets containing GEPDM was also reported.

4.1 Preparation and grafting properties of GEPDM

The GEPDM was prepared by solution graft copolymerization. The optimum reaction condition was reported by Fu et al. (2008) as shown in Table 3.1. The graft product was extracted by light petroleum ether (LPE) for 24 h by using soxhlet extraction for removing free rubber content and then dried to constant weight. To remove free copolymer, the dried residue was extracted by MEK/acetone (50/50 %v/v) for 24 h. The data obtained from all steps were used to calculate the percentage of conversion, grafting efficiency (GE) and grafting properties. The example for all calculations is shown in Appendix B. The grafting properties of GEPDM after extraction are shown in Table 4.1.

Table 4.1 Properties of graft copolymerization of MMA and ST onto EPDM

Reaction conditions				Grafting properties			
Temperature (°C)	Rubber concentration (wt%)	Time (h)	% conversion	% Free rubber	% Free copolymer	% Graft copolymer	%GE
80	8	12	33.2	78.9	10.4	10.7	57.3
90			34.1	80.0	7.98	12.0	68.7
90	6	12	24.6	78.3	11.5	10.1	41.6
	8		34.1	80.0	7.98	12.0	68.7
	10		26.6	81.0	11.4	7.52	45.5
90	8	4	20.6	80.1	15.3	4.58	10.4
		6	25.8	78.0	16.8	5.20	17.8
		8	28.6	75.3	18.1	6.65	18.7
		10	33.2	79.1	9.97	11.0	60.0
		12	34.1	80.0	7.98	12.0	68.7
		16	46.4	83.2	3.78	13.0	88.1
		20	51.8	81.0	11.5	7.53	66.4

For the effect of reaction temperature, it was found that the higher reaction temperature promoted the higher %conversion, %graft copolymer and grafting efficiency (%GE). It has been reported that both the graft polymerization rate and the copolymerization of ST and MMA increased with a rising polymerization temperature due to the enhancement of reactivity of rubber substrate, initiator and monomers and the reduction of rubber solution viscosity (Sheng et al., 1996 and Fu et al., 2008).

The effect of rubber concentration, the results showed that the %conversion, %graft copolymer and %GE increased with increasing rubber concentration from 6 wt% to 8 wt% since the chance of copolymerization between grafting sites and monomer radicals increased with increasing reactant concentration. However, overdose of rubber concentration caused the difficulty of the diffusion and mobility of monomer and free radicals of growth chains due to the higher viscosity. This decreased the rate of copolymerization and possibly promoted the formation of ungrafted copolymer (Fu et al., 2008). To obtain the highest % graft copolymer and % conversion, the suitable rubber concentration was 8 wt% of EPDM for graft copolymerization.

For the effect of reaction time, the % grafting copolymer and %GE rapidly increased with increasing reaction time to 16 h and then they tended to decrease when the reaction was leaved for 20 h. It can be explained that the ratio of the grafted monomer to copolymeric monomer increased at the initial period of reaction enough reactive sites on the EPDM chain resulting to the increase in the % graft copolymer and %GE. When the reaction time was 16 h, the EPDM chains were saturated with the grafting copolymeric chains. Above this point, the viscosity of the reaction solution increased with reaction time to obstruct the diffusion of monomer to react with EPDM (Hoang et al., 2000).

4.2 Structure characterization of GEPDM

After soxhlet extraction, GEPDM consisted of free EPDM, free copolymers and graft copolymers. Ungrafted PMMA, PS and poly(ST-*co*-MMA) are referred to as free copolymers. Grafted copolymers are referred as EPDM-*g*-PMMA, EPDM-*g*-PS, and EPDM-*g*-PMMA/ST.

4.2.1 Characterization of GEPDM using FT-IR spectroscopy

The functional groups in the EPDM rubber and its graft product were identified by FT-IR spectroscopy. Figure 4.1a and 4.1b show the FT-IR spectra in the region of 500-4000 cm^{-1} for EPDM rubber and grafted EPDM, respectively. The FT-IR spectrum of EPDM rubber exhibited the characteristic absorption band of C=C stretching vibration at 1680 cm^{-1}, the CH_2 vibration at 1449, the CH_3 vibration at 1376 cm^{-1} and the C=C bending vibration at 853 cm^{-1}. The new peaks in the FT-IR spectrum of GEPDM are the absorption bands of C=O stretching vibration of MMA at 1700 cm^{-1}. The sharp peaks at 700 and 1492 cm^{-1} are assigned to the aromatic rings. The board peak ranging between 3100-2960 cm^{-1} is due to the presence of the stretching vibration of C-H of ethylene norbornene. The FT-IR spectrum of GEPDM after soxhlet extraction confirmed that the PMMA and PS was "grafted from" the EPDM through the double bond during free-radical copolymerization.This indicated the occurrence of grafting of MMA and ST onto EPDM rubber (Lin-vien, 1991 and Colthup, Daly and Wiberley, 1964).

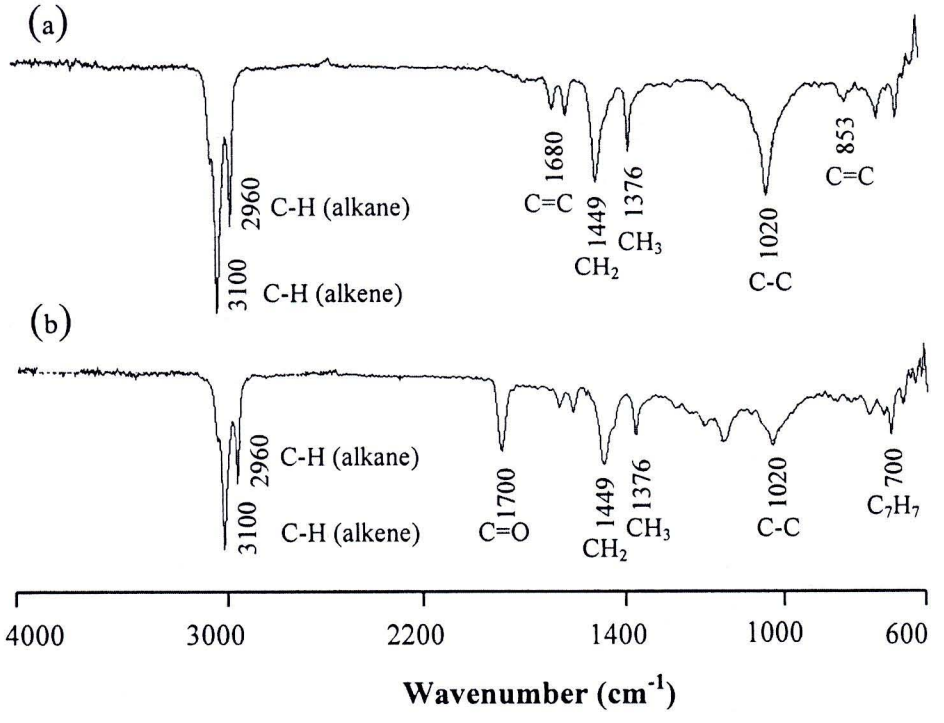


Figure 4.1 FTIR spectra of (a) EPDM and (b) GEPDM after soxhlet extraction.

4.2.2 Characterization of GEPDM using ^{1}H-NMR spectroscopy

Figures 4.2a and 4.2b present a comparison of the ^{1}H-NMR spectra of EPDM and GEPDM after soxhlet extraction. Figure 4.2 a shows the chemicals shift at 5.2 ppm attributed to the olefinic proton (=CH) in the EPDM rubber. All EPDM protons appear at chemical shift ranging from 0.7 to 1.3 ppm to CH_3 and CH_2 in the propylene units. Figure 4.2b shows the ^{1}H-NMR spectrum of GEPDM after soxhlet extraction. The spectrum exhibits a new peak appearing at 3.40 ppm refered to the methoxyl group (CH_3O) in PMMA. The peak at 2.1 ppm is due to the methylene in EPDM. The signals at 6.9-7.1 ppm are attributed to the phenyl group of PS (Fu et al., 2008).

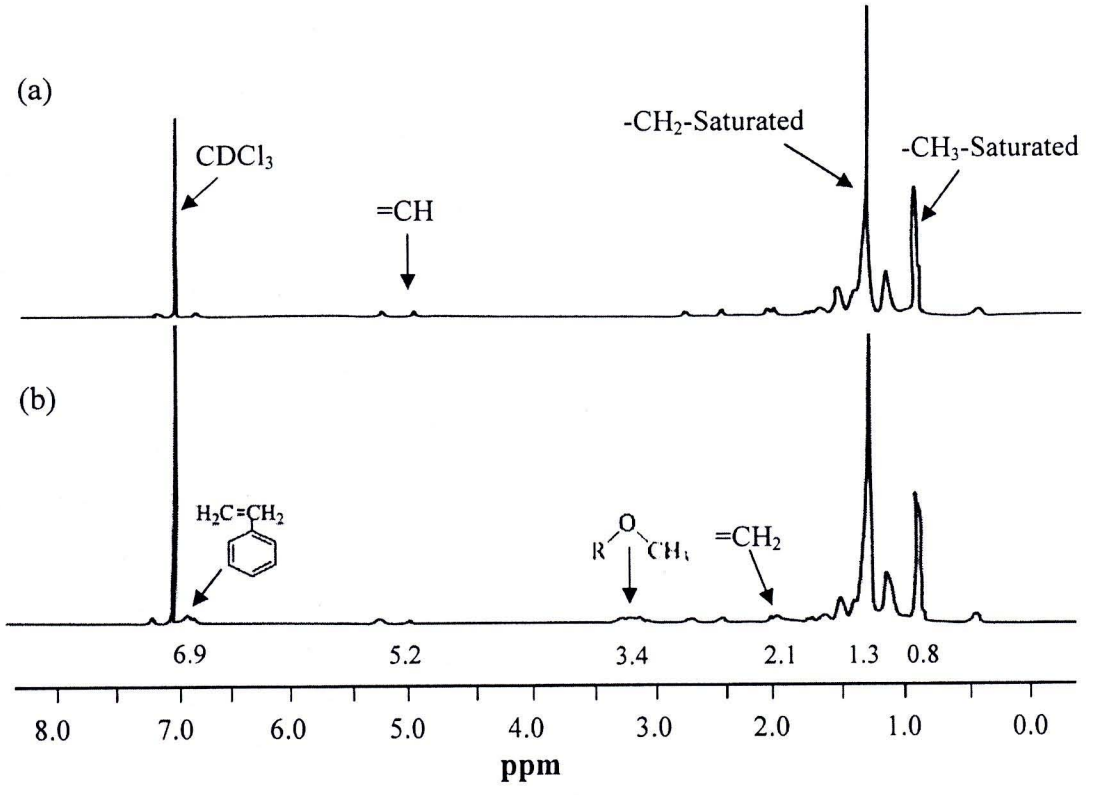


Figure 4.2 ^{1}H-NMR spectra of (a) EPDM and (b) GEPDM after soxhlet extraction.

4.3 Physical and mechanical properties of modified acrylic sheets containing GEPDM content

In this section, the physical and mechanical properties of the modified acrylic sheets containing GEPDM (88.1% GE) were investigated. This result was also compared to ones containing EPDM.

4.3.1 Transparency of modified acrylic sheets containing various GEPDM contents

Table 4.2 and Figure 4.3 show the appearance and color of the modified acrylic sheets containing GEPDM with various %GE and contents. For the effect of GEPDM content, it was found that the modified acrylic sheets still exhibited the transparent property when GEPDM content was in the range of 1.0–2.0 wt% (Figure 4.3c and 4.3d). Above these points, the modified acrylic sheets showed slight

opacity (Figure 4.3e and 4.3f). To compare with the modified acrylic sheet containing 1.0 wt% of EPDM (Figure 4.3b), the modified acrylic sheet was quite opaque. This indicated that the addition of EPDM and the overdose of GEPDM caused the higher opacity of the modified acrylic sheets due to the phase separation effect.

For the effect of %GE (Table 4.2) on the appearance of the modified acrylic sheets having 2.0 wt% of GEPDM, the result indicated that the increase in the %GE of GEPDM from 10.4 to 88.1% decreased the phase separation effect resulting to the reduction of opacity of the modified acrylic sheets.

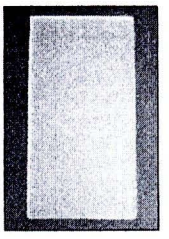
Table 4.2 Appearence of modified acrylic sheets containing various rubber content and %GE.

Sample	Rubber content (wt%)	GE (%)	Sheet appearance
Acrylic sheet*	-	-	transparent
Acrylic sheet/EPDM	1.0	-	quite opaque
Acrylic sheet/GEPDM**	1.0	88.1	transparent
	2.0		transparent
	3.0		little opaque
	4.0		little opaque
	2.0	10.4	quite opaque
	2.0	17.8	quite opaque
	2.0	18.7	quite opaque
	2.0	60.0	little opaque
	2.0	68.7	little opaque
	2.0	88.1	transparent

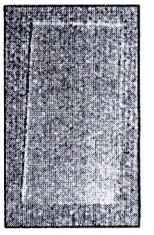
* Acrylic sheet (MMA/ST=80/20 %w/w)

** GEPDM (88.1% GE)

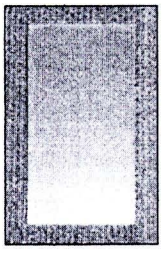
(a) Acrylic sheet (MMA/ST=80/20 %w/w)



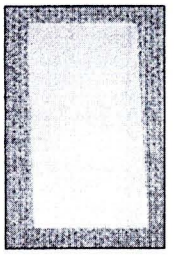
(b) 1.0 wt% EPDM



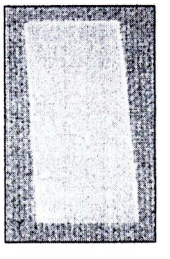
(c) 1.0 wt% GEPDM



(d) 2.0 wt% GEPDM



(e) 3.0 wt% GEPDM



(f) 4.0 wt% GEPDM

Figure 4.3 Transparency of modified acrylic sheets containing various GEPDM rubber contents.

4.3.2 Mechanical properties of the modified acrylic sheets

The influence of the %GE and content of GEPDM on the mechanical properties of the modified acrylic sheets was shown in Figure 4.4 and Figure 4.5, respectively. The results were compared to the acrylic sheet (MMA/ST=80/20 wt%) without modification and one containing EPDM. For the addition of 1.0 wt% of EPDM, the modified acrylic sheet exhibited the significant reduction of flexural strength (Figure 4.4b), tensile strength (TS) (Figure 4.4c) and elongation at break (EB) (Figure 4.4d) possibly due to the phase separation resulting from the dissimilar polarity of EPDM and monomer mixture used for preparing the acrylic sheets. However, the addition of EPDM did not affect the impact strength of the modified acrylic sheets (Figure 4.4a). It could be explained that EPDM retained the impact strength of the modified acrylic sheet due to its good rebound property.

For the addition of GEPDM at various contents, it was found that the impact strength (Figure 4.4a), flexural strength (Figure 4.4b) and TS (Figure 4.4c) of the modified acrylic sheets were higher than those of one containing EPDM at the same content. The reduction of EB value of the modified acrylic sheet containing GEPDM also exhibited the higher crosslink density. This implied that GEPDM had the higher compatibility with MMA/ST monomer mixture resulting to the better mechanical properties of the modified acrylic sheet. The obtained experimental result were similar to the previous literature that use, the graft product-based elastomer as the compatibilizer for the blends containing constituents with different polarity (Kraus, 1978). However, Figure 4.4 shows the decrease in the flexural strength, TS and EB when the amount of GEPDM was higher than 2.0 wt%. It was due to the interfacial saturation of GEPDM in the thermoplastic components. The similar results were also observed in the natural rubber/PMMA blends compatibilized by natural rubber grafted with glycidyl methyl methacrylate (Suriyachai et al., 2004). Moreover, the overdose of GEPDM caused the high level of EPDM content in the system providing the phase separation.

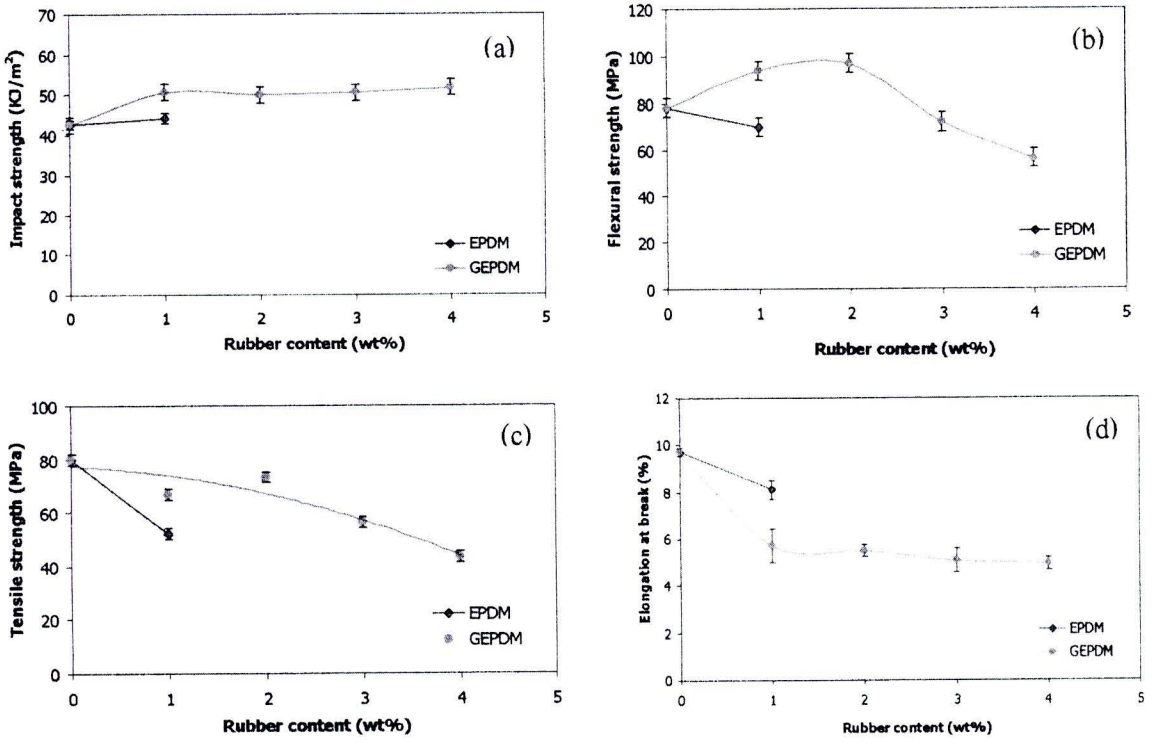


Figure 4.4 Effect of GEPDM content (%GE=88.1) on the mechanical properties of the modified acrylic sheets.

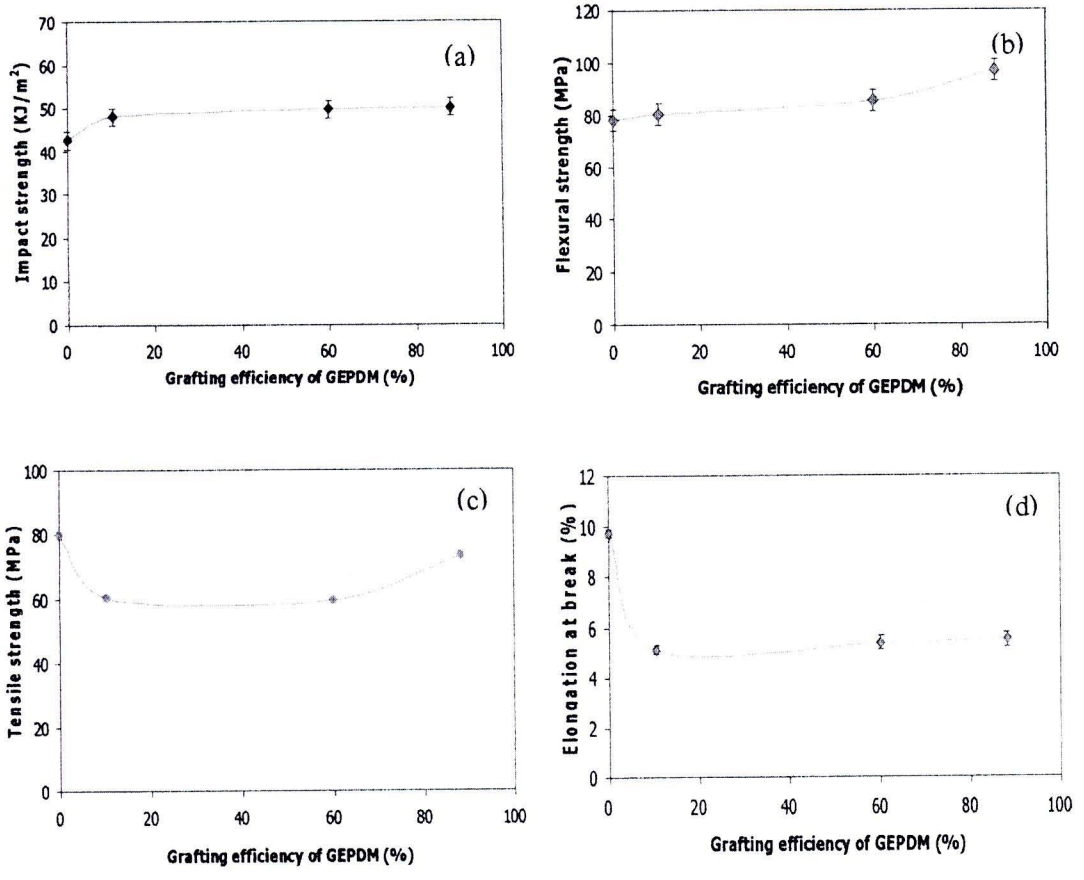


Figure 4.5 Effect of %GE on the mechanical properties of the modified acrylic sheets containing 2 wt% of GEPDM.

It was noticed that the TS and EB values of the modified acrylic sheets containing GEPDM at any content were lower than those of the acrylic sheet without the addition of GEPDM. It was due to the low tensile properties of EPDM with more brittle property after graft copolymerization of ST and MMA onto EPDM.

For the effect of %GE (Figure 4.5), it indicated that the addition of GEPDM at 2 wt% into the MMA/ST mixture gave the higher impact strength, flexural strength and tensile properties with increasing the %GE of GEPDM. This could be explained that the increase in the %GE of GEPDM promoted the higher compatibility to improve the interfacial adhesion between GEPDM and MMA/ST monomer matrix.

The stress-strain behavior of the modified acrylic sheets after tensile test is shown in Figure 4.6. The stress-strain curve of the modified acrylic sheet

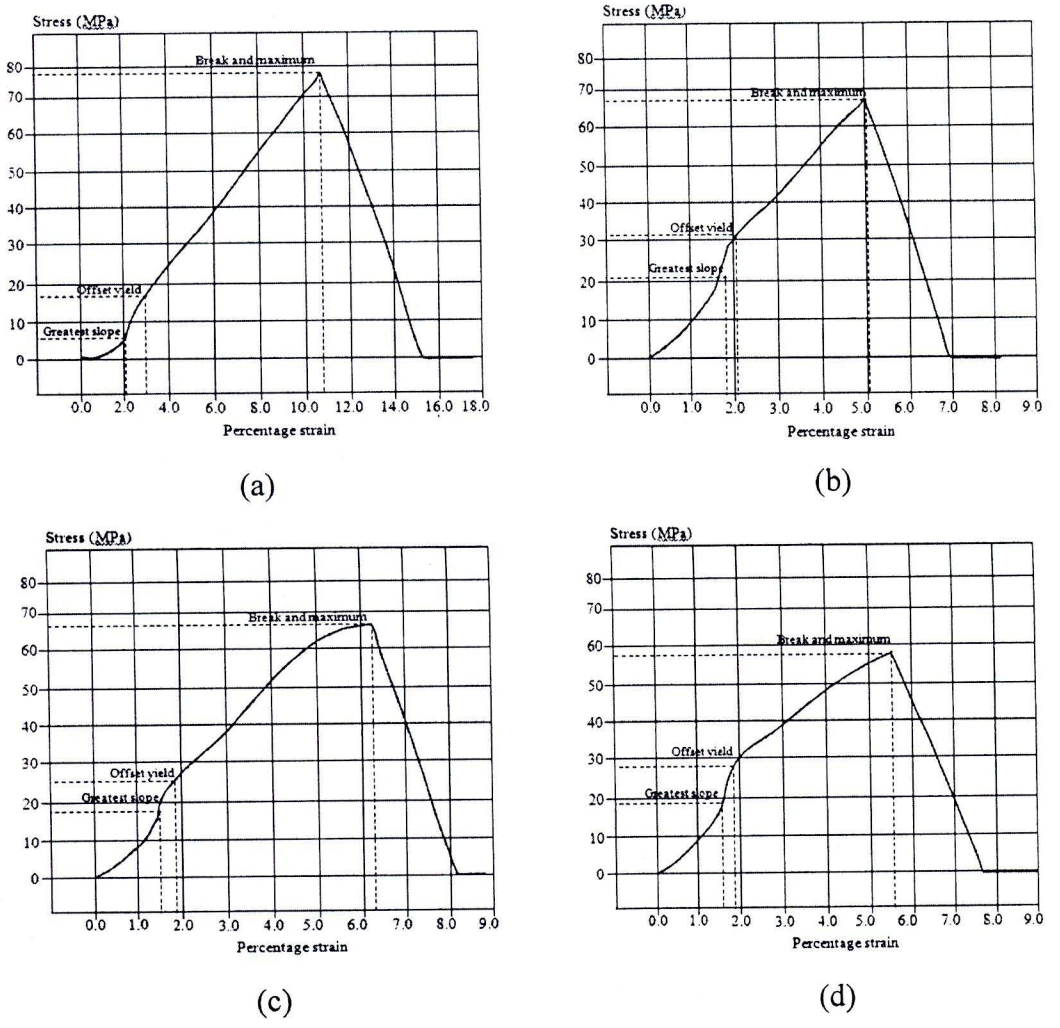


Figure 4.6 Stress-strain behavior of the acrylic sheets: (a) without GEPDM, (b) with 1 wt% of GEPDM, (c) with 2 wt% of GEPDM and (d) with 3 wt% GEPDM.

without GEPDM showed the rigid or brittle characteristics with higher elongation (Figure 4.6a). The brittle property of the modified acrylic sheet was gradually shifted to be ductile property when the amount of graft copolymer increased as shown in Figure 4.6b-d. Therefore, the modified acrylic sheets with GEPDM showed a brittle-ductile transition behavior, whereas the neat PMMA/ST was the brittle material. Similar behavior was also observed in the strain-rate effect of EVA/PMMA *in situ* polymerization blends (Cheng et al., 2004). The stress-strain curve of the modified acrylic sheet with 4 wt% of GEPDM clearly exhibited the yield point and the low percentage of strain.

4.4 Morphology of the modified acrylic sheet

The scanning electron micrographs of the fracture surface of the acrylic sheets before and after modification by addition of EPDM or GEPDM Z (%GE = 88.1%) were shown in Figure. 4.7. It was found that the uncompatibilized acrylic sheet (Figure. 4.7a) exhibited the large cracking traces indicating the brittle behavior. For the addition of EPDM at 1.0 wt% (Figure. 4.7b), the fracture surface of the modified acylic sheet exhibited the heterogeneity with phase separation between EPDM and thermoplastic resulting to poor mechanical properties. To consider the addition of GEPDM into the MMA/ST monomer mixture, it was observed that the fracture surface of the modified acrylic sheets containing 1.0 wt% (Figure. 4.7c) and 2.0 wt% (Figure. 4.7d) became smoother which is the characteristics of the ductile materials. This implied that GEPDM could act as the interfacial agent to improve the mechanical properties of the modified acrylic sheets.

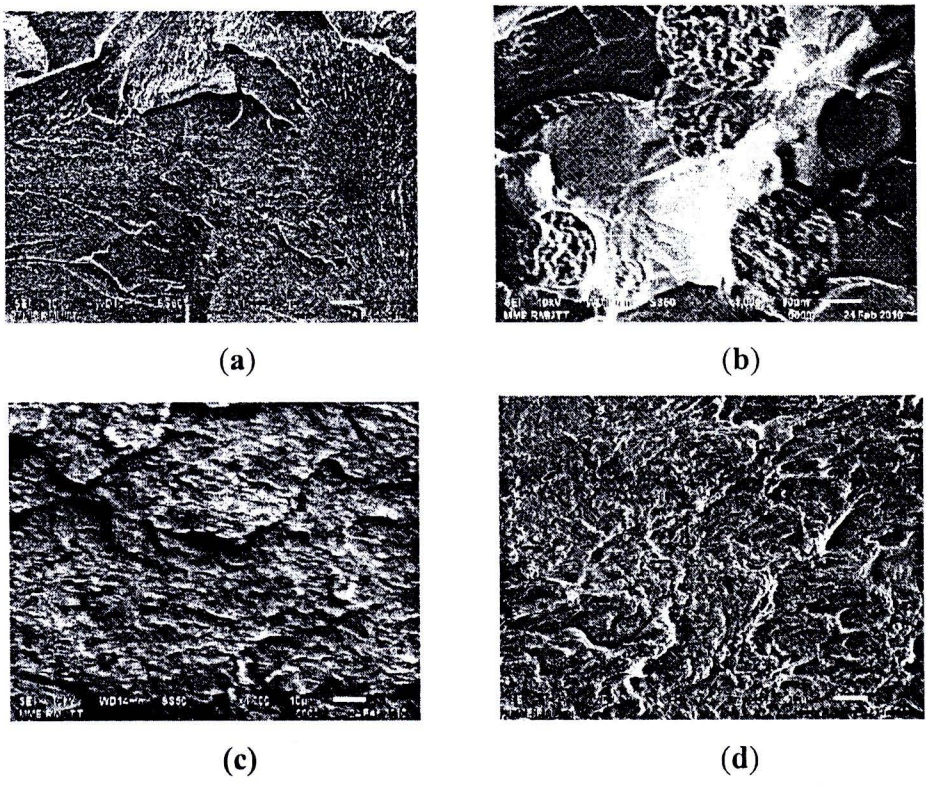


Figure 4.7 SEM micrographs of the acrylic sheets: (a) without modification, (b) addition of 1.0 wt% of EPDM, (c) addition of 1.0 wt% of GEPDM and (d) addition of 2.0 wt% of GEPDM (magnification x1000).

4.5 Thermal and UV aging of the modified acrylic sheet

In the previous section, it was found that the impact strength, flexural strength and tensile strength of the modified acrylic sheets were slightly improved by adding the small amount of GEPDM. However, it is necessary to investigate the ageing resistance of these modified acrylic sheets for outdoor application. The thermal and UV resistances of the modified acrylic sheets were examined and reported in the term of the mechanical properties retention.

4.5.1 Mechanical properties retention of modified acrylic sheets after aging

Figure 4.8 and Figure 4.9 show the effect of content and %GE of GEPDM, respectively on the retention of mechanical properties of the modified

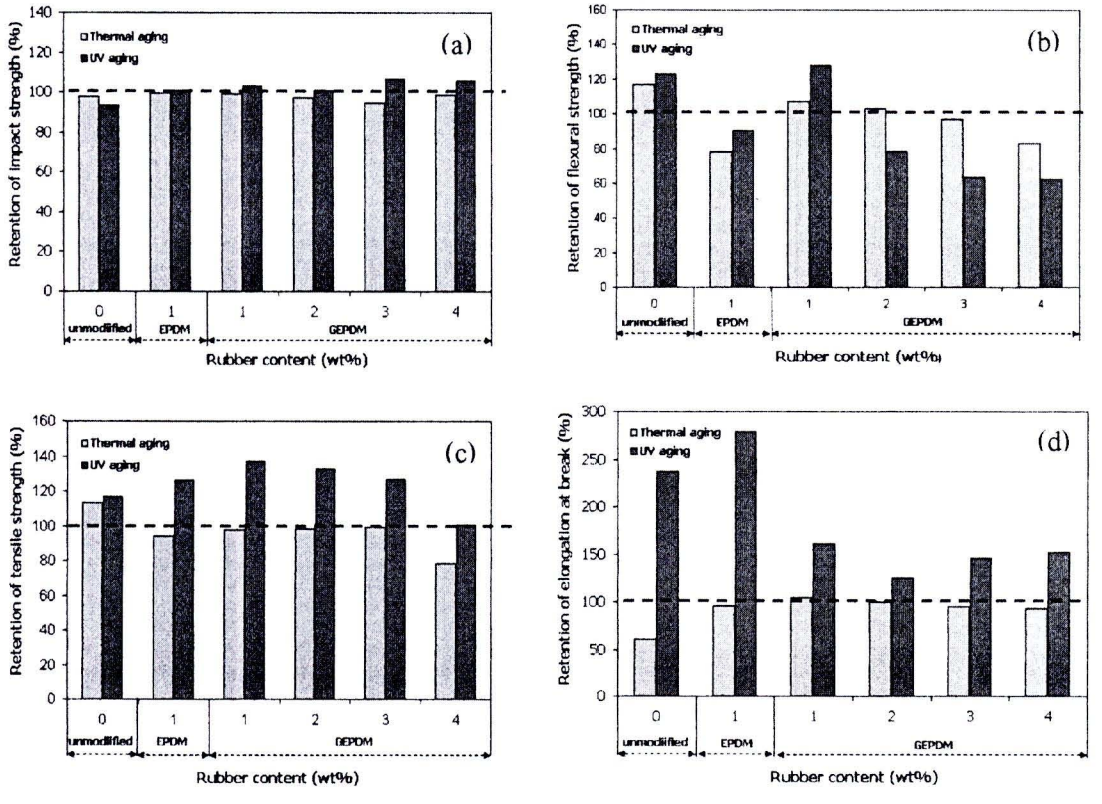


Figure 4.8 Effect of GEPDM content on the mechanical properties of the modified acrylic sheets after aging (%GE= 88.1%).

acrylic sheets after thermal and UV aging could retain and/or gave the better mechanical properties possibly due to the self polymerization during aging process. The thermal aging provided the higher flexural strength (Figure 4.8 b) and TS (Figure 4.8c) with lower EB (Figure 4.8d) resulting to the higher crosslink density. Moreover, the UV aging exhibited the good results for flexural strength, TS and EB of the acrylic sheet due to the penetration power of UV to promote the post polymerization inside the specimens. Thus, the UV aging or UV cure is generally applied for polymer used in the coating process such as polyurethane (Technical information, 2004).

For the addition of EPDM or GEPDM, the results in Figure 4.8a and 4.9a indicated that the modified acrylic sheet containing 1wt% of EPDM or GEPDM at various contents and %GEs could retained the impact strength after thermal and UV aging resulting from the EPDM segment with great thermal and UV resistance. However, at 1 wt% of rubber content, the modified acrylic sheets containing GEPDM had higher %retention of flexural strength and TS with lower EB than EPDM. It can be explained that the effect of higher compatibility was possibly promote the higher crosslink density inside the specimens. When %GE of GEPDM was kept constant at 88.1% (Figure 4.8), the increase in the GEPDM content reduced the retention of the mechanical properties of the modified acrylic sheets. This was possible that the higher rubber level promoted higher incompatibilization to inhibit the self-polymerization of MMA/ST monomer during thermal and UV aging. For the effect of %GE (Figure 4.9), it was found that the increase in the %GE of GEPDM also to decreased the thermal and UV resistance of the modified acrylic sheets due to the higher content of -C=O- functional group in GEPDM which was susceptible to heat and UV (Decker, 1996). It could be concluded that GEPDM content in the range of 1.0-2.0 wt% with 60-88.1% of %GE could retain and/or increased the mechanical properties of the modified acrylic sheet after thermal and UV aging.

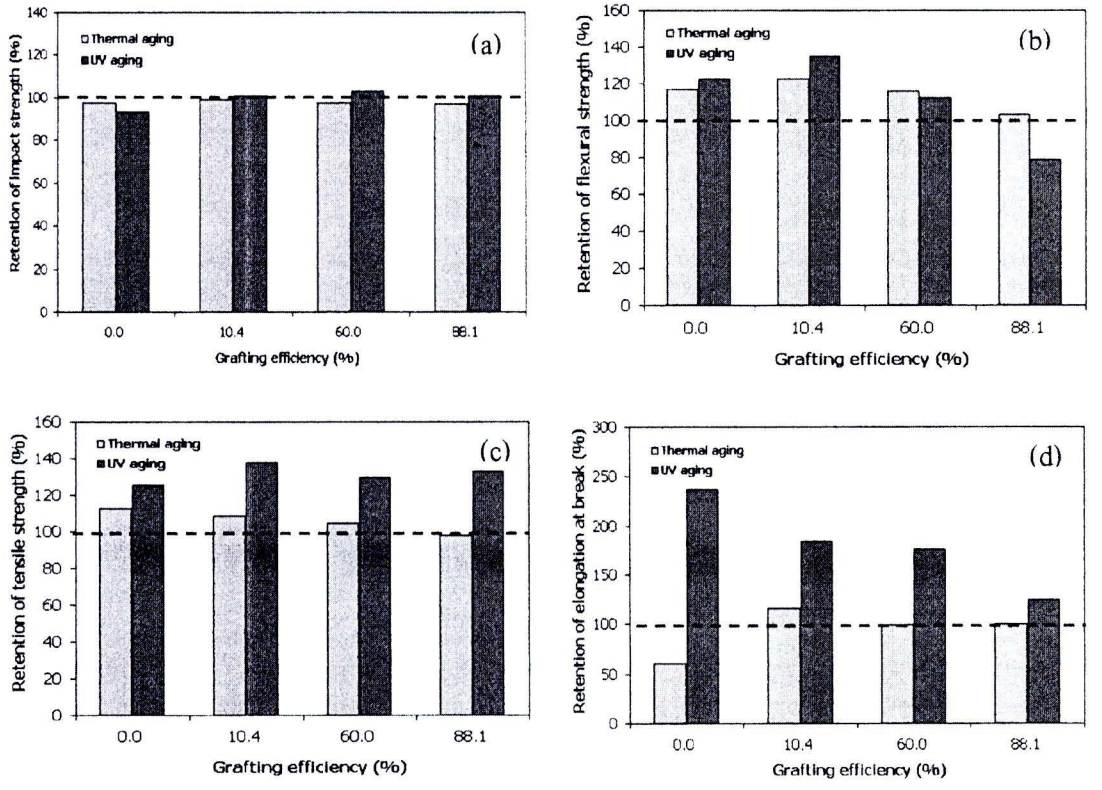


Figure 4.9 Effect of %GE of GEPDM (2 wt%) on the mechanical properties of modified acrylic sheets after aging.

4.5.2 Transparency stability of the modified acrylic sheets after aging.

Table 4.3 shows the effect of the GEPDM content and %GE of the modified acrylic sheet on the opacity value and color difference of the modified acrylic sheets after thermal and after UV aging. It can be seen that opacity of the modified acrylic sheets increased with increasing the GEPDM content. However, the opacity values of the modified acrylic sheets containing GEPDM were lower than that of one containing EPDM due to dissimilar polarity effect. This indicated the more compatibilization of GEPDM in the MMA/ST phase in the acrylic sheets.

Table 4.3 Physical properties of modified acrylic sheet

Sample	Rubber Content (wt%)	GE (%)	Opacity (%)	ΔE of thermal resistance	ΔE of UV resistance
Acrylic sheet*	-	-	12.63 ± 0.08	0.45 ± 0.09	10.35 ± 0.26
Acrylic sheet/EPDM	1.0		28.30 ± 0.45	2.56 ± 0.16	15.61 ± 1.40
Acrylic sheet/GEPDM**	1.0	88.1	16.74 ± 10.09	1.41 ± 0.05	11.97 ± 1.61
	2.0		18.39 ± 0.06	2.29 ± 0.12	12.24 ± 0.17
	3.0		21.94 ± 0.02	2.71 ± 0.10	16.01 ± 0.77
	4.0		21.74 ± 0.25	2.96 ± 0.23	15.82 ± 0.46
	2.0	10.4	28.72 ± 0.07	2.93 ± 0.18	14.55 ± 0.77
	2.0	17.8	26.22 ± 0.06	2.80 ± 0.11	14.57 ± 0.52
	2.0	18.7	23.42 ± 0.31	2.75 ± 0.16	14.70 ± 0.27
	2.0	60.0	23.49 ± 0.53	2.68 ± 0.37	12.73 ± 0.06
	2.0	68.7	18.67 ± 0.19	2.52 ± 0.15	12.44 ± 0.18
	2.0	88.1	18.39± 0.06	2.29 ± 0.12	12.24 ± 0.17

* Acrylic sheet (MMA/ST=80/20 %w/w)

** GEPDM (88.1% GE)

The thermal stability of the modified acrylic sheets was also examined by monitoring the yellowness of the test specimens, which can be reported in the term of ΔE. The effects of GEPDM content and %GEs on the ΔE of the specimens are shown in Table 4.3. It can be seen that ΔE of the modified acrylic sheets increased with increasing the GEPDM content possibly due to the higher incompatibilization. (Pinheiro et al., 2004). The ΔE of modified acrylic decreased with increasing %GE. It was explained that the increase of %GE increased the compatibility between GEPDM and modified acrylic sheet. To compare with the modified acrylic sheet containing EPDM, the thermal resistance of one containing GEPDM was better than that of a one containing EPDM. Due to the phase separation resulting from dissimilar polarity between EPDM and MMA/ST used for preparation of the acrylic sheets.

The ultraviolet stability the modified acrylic sheets was also examined by monitoring the yellowness shifts which are reported in the term of ΔE. It can be seen that the ΔE value of modified acrylic sheet with increasing the GEPDM content.

However, the increase in the %GE of GEPDM reduced the ΔE value of the modified acrylic sheets. It can be explained by the double bond in the EPDM, MMA and ST structure. Selective incorporation of UV sensitive molecular structures such as vinyl groups and non-addition of photosensitizers could promote the photodegradation. (Saechtling, 1995). It could be notice that the color stability of the modified acrylic sheets containing GEPDM after UV aging was slightly higher than that of a one containing EPDM.

4.6 Thermal properties of modified acrylic sheet

4.6.1 Differencial scanning calorimetry, DSC

Differential scanning calorimetry (DSC) can be used for evaluation of the miscibility between components of copolymers. In the absence of miscibility, a polymer blend of two polymers exhibits two distinct glass transition temperature (Tg) of the pure components. Figure 4.10 shows the DSC thermograms of the EPDM, GEPDM (88.1%GE) and acrylic sheets (MMA/ST = 80/20 %w/w) with and without the addition of GEPDM (%GE = 88.1%) (1-4 wt%).

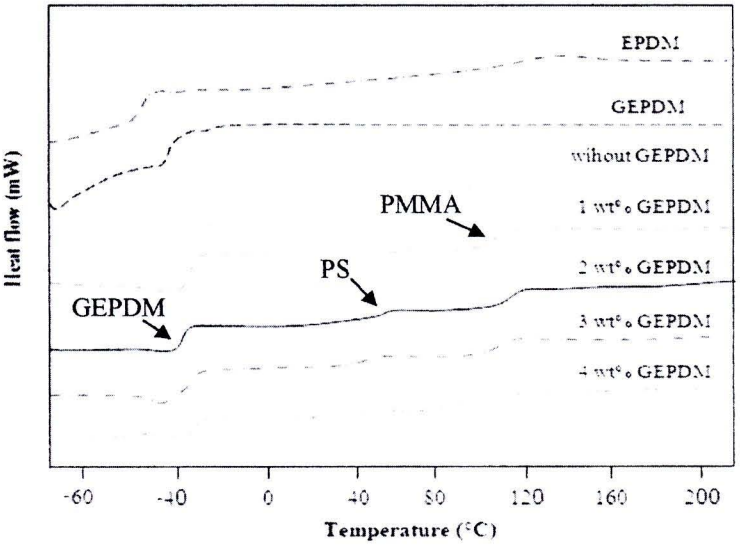


Figure 4.10 DSC thermograms of EPDM, GEPDM and acrylic sheet with and without the addition of GEPDM at various contents.

Table 4.4 summaries T_g of all samples. It was found that EPDM was shifted from -52.9°C to -40.3°C due to higher rigidity of EPDM after graft copolymerization of ST and MMA which are the monomers for producing the brittle materials. For the acrylic sheet without the addition of GEPDM, the DSC thermogram indicated two T_g values at 110°C and 73.3°C attributed to PMMA and PS phases, respectively (Silva et al., 2004). When GEPDM was added, the DSC thermograms exhibited three T_g values due to EPDM, PMMA and PS of the modified acrylic sheets. The result showed the shift of T_g values from the unmodified acrylic sheets indicating the partial compatibilization from the addition of GEPDM. It can be seen that the increase in the GEPDM content increased the T_g values of EPDM phases due to the higher rigidity resulting from the graft copolymerization as explained above. For PMMA and ST phases, the addition of 1.0-2.0 wt% of GEPDM reduced T_g from 110°C to 108°C for PMMA and 73°C to 72°C for PS resulting from the soft segment of EPDM in GEPDM. However, the increased in the GEPDM above this point increased T_g value of PMMA which was close to that of unmodified one. This result was opposited to the PS phase. This is possible that GEPDM was more compatible to PS phase than PMMA phase in the modified acrylic sheet.

Table 4.4 T_g values of modified acrylic sheet prepared by addition of GEPDM with various GEPDM contents

Sample	Rubber content in acrylic sheet (wt%)	T_g of each polymeric phases (°C)		
		EPDM	PMMA	PS
EPDM	-	-52.9	-	-
GEPDM*	-	-40.3	-	-
Acrylic sheet**	-	-	110.0	73.3
Acrylic sheet/GEPDM	1.0	-41.5	108.2	71.0
	2.0	-41.6	108.3	71.9
	3.0	-41.0	109.3	66.4
	4.0	-39.6	111.0	65.1

* GEPDM (88.1 %GE)

** Acrylic sheet (MMA/ST=80/20 %w/w)

4.7 Kinetic study of thermal degradation

4.7.1. EPDM and GEPDM

Thermogravimetric analysis is one common technique to evaluate the thermal stability of materials, and also indicate the decomposition of polymers at various temperatures. Thermal stability can be regarded as the ability to maintain the required properties of materials at a desired temperature. Figure 4.11 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of EPDM and GEPDM (%GE = 88.1%) in the presence of a nitrogen atmosphere. The initial decomposition temperature (T_{id}), the decomposition temperature at the maximum weight loss rate (T_p) and the final decomposition temperature (T_f) are summarized in Table 4.5. It indicated that the thermal decomposition of rubbers was an overall one-step reaction because the TG curve of the samples was one-step and provided smooth weight loss curves. The initial decomposition temperature of EPDM (415.9°C) was higher than that of GEPDM (287.2°C). It indicated that GEPDM had lower thermal stability than EPDM due to the –C=O- functional group in GEPDM which was susceptible to thermal degradation (Hinchiranan et al., 2009). However, it was found that the DTG curve (Figure 4.11b) of EPDM had higher maximum weight loss rate than that of GEPDM. This means that EPDM was rapidly decomposed at temperature above 496.9°C, although the saturation backbone provides the highest decomposition temperature.

The activation energy (Ea) of pure EPDM and GEPDM calculated using the Kissinger method are obtained from the slope of the plot between $\ln(\beta / T_p^2)$ versus $1/T_p$ (Kissinger, 1702) from room temperature to 600°C at 2.5, 5 and 10°C/min in nitrogen atmosphere as shown in Figure 4.12. From Table 4.5,

Table 4.5 Decomposition temperatures, maximum weight loss rate and activation energy of thermal decomposition under N_2 atmosphere of EPDM and GEPDM

Sample	Decomposition temperature (°C)*			$(d\alpha / dt)_p$ ** (%/min)	E_a (kJ/ mol)
	T_{id}	T_p	T_f		
EPDM	415.9	461.6	496.9	35.17	222.5
GEPDM	287.2	459.4	493.9	23.60	274.5

* Recorded at 10 °C/ min of heating rate.

** $(d\alpha / dt)_p$ = maximum weight loss rate

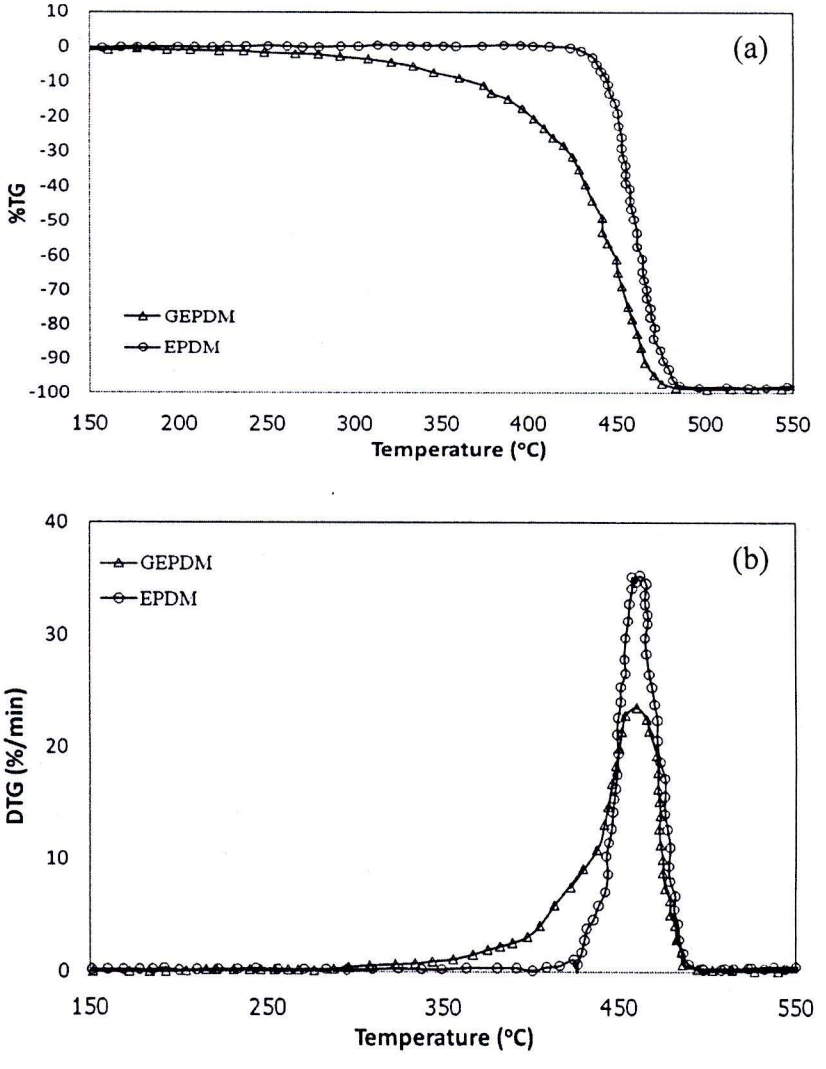


Figure 4.11 Thermogravimetric curves of GEPDM and EPDM at a heating rate of 10°C/min under nitrogen atmosphere : (a) TG and (b) DTG curves.

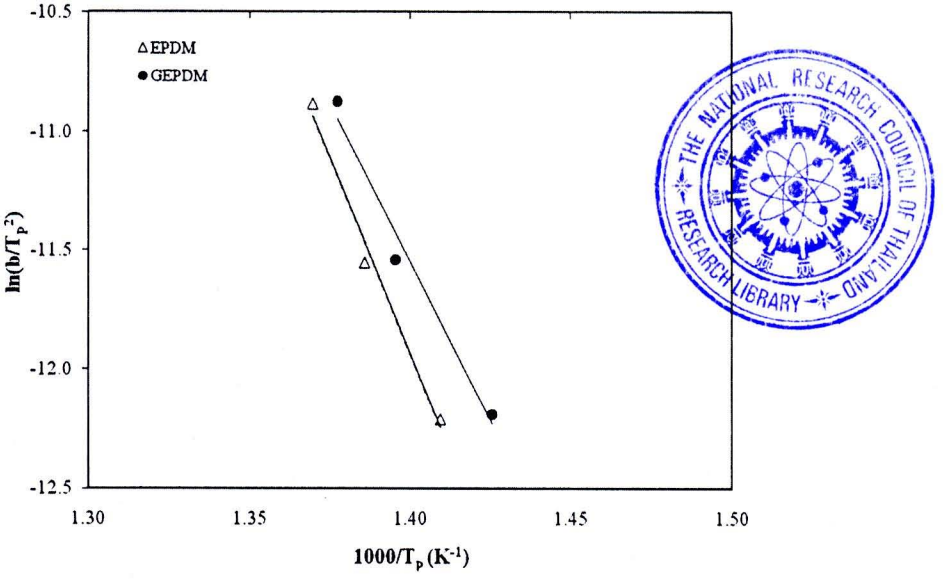


Figure 4.12 Plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ at various heating rates: (Δ) EPDM and (•) GEPDM.

the E_a of GEPDM (274.5 kJ/mol) was significantly higher than that of EPDM (222.5 kJ/mol). This implies that GEPDM required more energy to break down the chemical bond due to the PS units in the GEPDM which had high thermal stability resulting from benzene ring in the structure (Kannan et al., 2009).

4.7.2. Modified acrylic sheets

Under nitrogen atmosphere, the effect of the addition of GEPDM (88.1%GE) at various contents on the decomposition temperature and activation energy of thermal decomposition of modified acrylic sheet (MMA/ST = 80/20% w/w) was presented in Figure 4.13 and Table 4.6. Figure 4.13 shows the two-stage thermal decomposition pattern of unmodified acrylic sheet and one-stage decomposition of the modified acrylic sheet with containing GEPDM. From the DTG curve (Figure. 4.13b), the one stage and two stage of the decomposition of unmodified acrylic sheet (Hu et al., 2003) were appeared at a peak temperature (T_p) around 275.9°C and of 360.3°C, respectively. The thermal decomposition referred to the decomposition of PMMA (Madras et al., 1795) and the second decomposition stage was the decomposition of PS (Silva et al., 2004, Karmore et al., 2000). The addition of GEPDM shifted the two-stage decomposition of the acrylic sheet to the one-stage decomposition. This

indicated the higher compatibility of GEPDM and the MMA/ST monomers used for preparation of the modified acrylic sheets. It was observed that the increase in the GEPDM content promoted the higher T_p due to the effect of EPDM segment in the GEPDM. This means that the modified acrylic sheets had higher thermal resistance than unmodified ones. However, the overdose of GEPDM caused the reduction of T_{id} possibly due to the higher incompatibility and GEPDM might be partially decomposed at the initial decomposition process.

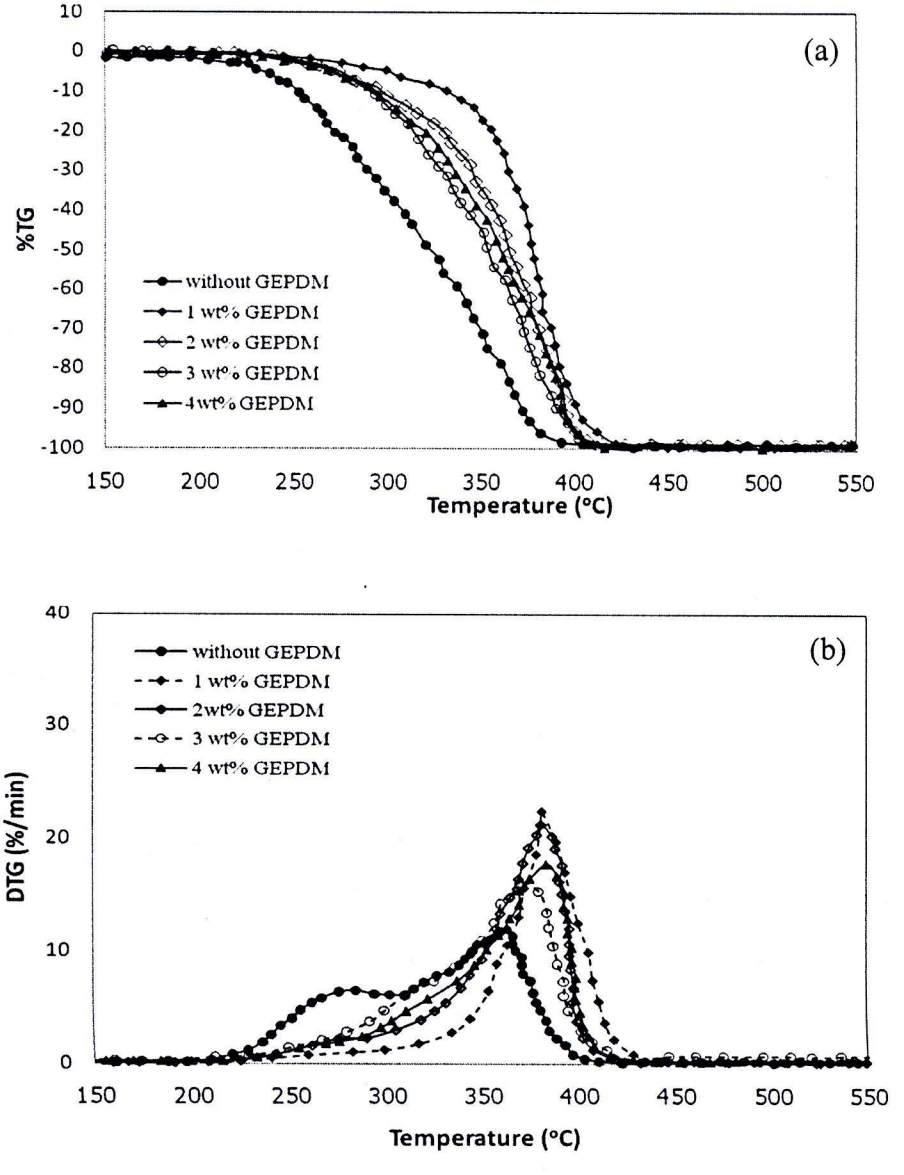


Figure 4.13 Thermogravimetric curves of the modified acrylic sheets containing various GEPDM content at heating rate of 10°C/ min under nitrogen atmosphere: (a) TG and (b) DTG curves.

Table 4.6 Decomposition temperatures, maximum weight loss rate and activation energy of thermal decomposition under N_2 atmosphere of the modified acrylic sheets with and without the addition of various GEPDM

Sample	Rubber content (wt%)	Decomposition temperature (°C)*			$(d\alpha/dt)_p$** (%/min)	E_a (kJ/ mol)
		T_{id}	T_p	T_f		
Acrylic sheet***						
first stage	-	209.4	275.9	310.7	6.54	183.4
second stage	-	310.7	360.3	410.6	11.78	40.8
Acrylic sheet/GEPDM****	1.0	240.6	382.0	439.9	22.42	210.7
	2.0	224.4	381.5	431.9	21.23	108.5

* Recorded at 10 °C/ min of heating rate.

** $(d\alpha/dt)_p$ = maximum weight loss rate

*** Acrylic sheet (MMA/ST=80/20 %w/w)

**** GEPDM (88.1 %GE)

The activation energy (E_a) of the modified acrylic sheets containing GEPDM (%GE = 88.1%) at various contents was also calculated using the Kissinger method at heating rate of 2.5, 5 and 10°C/min under nitrogen atmosphere as shown in Table 4.6. For the unmodified acrylic sheet, the activation energy of the first stage was higher than that of the second stage because PS is a more stable matrix which shows degradation in a single stage (Silva et al., 2004 and Madras, 1997). When 1.0 wt% of GEPDM was applied to the modified acrylic sheets, the E_a of thermal decomposition of the modified acrylic sheet was increased to 210.7 KJ/mol which was higher than that of the unmodified one. It could be explained that the EPDM segment in GEPDM enhanced the thermal resistance of the modified acrylic sheet. However, it was observed that the E_a value the modified acrylic sheets decreased with increasing the GEPDM content possibly due to the incompatibilization effect that might reduce the E_a value resulting in the ease of thermal decomposition (Awad, 1999, Nishikawa, 1999 and Srinivas, 1994).