CHAPTER IV

TRANSESTERIFICATION OF ETHYLNE(VINYL ACETATE) BY CATALYTIC REACTIVE EXTRUSION IN AN INTERMESHING CO-ROTATING TWIN-SCREW EXTRUDER

4.1 Abstract

Transesterification of ethylene (vinyl acetate) or EVA was done in a 20-mm diameter twin–screw extruder with 20:1 L/D ratio, via catalytic reactive extrusion with various screw rotating speeds. The conversion of modified ethylene (vinyl acetate) at each screw rotating speed was examined by solvent extraction and Fourier Transform Infrared Spectroscopy (FTIR). The thermal properties, and dynamic mechanical properties of the modified ethylene (vinyl acetate)s were also investigated.

The results from dynamic mechanical test revealed that the lower screw rotating speed gave the higher tan δ with the lower loss modulus, which could be implied that hydroxyl substitution was achieved and hydrogen bonding was occurred.

4.2 Introduction

Ethylene(vinyl acetate) or EVA, with characteristic properties such as toughness and flexibility are useful to modify the rigid and brittle polymers like polylactid or PLA, in order to enhance processibility and/or flexibility of PLA by grafting PLA onto EVA chains [1].

Graft copolymerization of PLA onto EVA chains, EVA needs to have hydroxyl groups along the chains to facilitate the graft copolymerization reaction [2]. Therefore, functional group modification of EVA was carried out and transesterification of EVA with alcohol by catalytic reactive extrusion was the preferable route [3,4].

Transesterification of EVA with alcohol by catalytic reactive extrusion, where the reaction takes place inside the extruder with the help of catalyst, was the preferable route to make it more polar and miscible with polar polymers in blending and/or grafting systems provided versatility of EVA throughputs [5,6].

In this work, the suitable screw rotating speed giving the highest conversion was examined. Moreover, thermal properties and dynamic mechanical properties of the modified EVA were also investigated.

4.3 Experimental

A mixture of 300g of EVA (TPI POLENE), 40ml of 1-dodecanol and 0.5%wt of dibutyltin dilaurate (DBTDL) [7] purchased from SM Chemicals (Sigma Aldrich), were mixed together in a container then fed into a twin-screw extruder (LabTech), with 2 die exits (3-mm diameter). The operating temperatures of 10 zones from hopper to die were 145-165-175-180-185-185-185-185-185-190 °C. The screw rotating speeds were varied, i.e. 10, 20, 30, and 40 rpm. The throughput was collected and dried, and mixed again by the same condition to increase the reaction time. Then the throughput was extracted by acetone to get rid of excess 1-dodecanol and dried in vacuum oven at 30°C for several hours before shaped into thin film by compression moulding (Wabash) at 120°C (preheat 10 minutes and compress 5 minutes), in order to examine the conversion of EVA to EVA-co-EVOH (or modified EVA) by FTIR (Nexus 670, Thermo Nicolet). The thermal properties were carried out by DSC (Mettler Toledo, DSC822), samples were being heated from -30 °C to130 °C and cooled to -30 °C, then heated again from -30 °C to130 °C with heating rate 5 °C/min while TGA (Perkin Elmer, Pyris Diamond) providing thermal stabilities of the modified EVAs ran in temperature range of 30-800 °C with heating rate 10 °C/min. Dynamic mechanical properties of the modified EVAs were also investigated using NETZSCH DMA 242, penetration mode from -100 °C to 40 °C, sample size 5mm × 5mm × 3mm (width×length×depth), amplitude 30.0 μm, and frequency 1 Hz.

4.4 Results and Discussion

4.4.1 Extrusion

Considering the modified EVA in Figure 4.1, the appearance of the pure EVA; and modified EVA at 10, 20, 30, and 40 rpm; respectively. All of the

modified EVA did not show the significant difference. The retention time of the throughput at each screw speed is shown in Table 4.1.

Figure 4.1 Appearance of pure EVA; and modified EVA at 10, 20, 30, and 40 rpm from twin-screw extruder.

Table 4.1 Retention time and Mass throughput of each screw speed

Screw speed (rpm)	Retention time (min)	Throughput rate (g/hr)
10	11.36	166.02
20	6.44	213.12
30	3.47	871.86
40	1.45	973.38

4.4.2 Solvent Extraction of modified EVA

Conversions of the modified EVA were studied by solvent extraction with acetone at 160 °C in order to wash out the excessive 1-dodecanol. The insoluble parts were vacuum dry at 60 °C overnight, %yields of modified EVA were calculated from dry weight of insoluble product. The modified EVA at 20 and 30 rpm give the most appropriate conversion, as shown in Table 4.2.

%yield = [Wt. of insoluble product (g) / Wt. of crude product (g)] × 100   (4-1)

Table 4.2 Conversions of the modified EVA at various screw speeds

Sample	Crude product (g)	Insoluble product (g)	%yield	%unreacted alcohol	Conversion (mol%)
mEVA 10 rpm	3.2585	2.7832	85.41	14.59	28.412
mEVA 20 rpm	3.3215	2.9009	86.99	13.51	28.772
mEVA 30 rpm	3.4008	2.9116	87.34	12.66	29.055
mEVA 40 rpm	3.3301	2.8969	85.62	14.58	28.416

4.4.3 FTIR Analysis of modified EVA

The insoluble parts from solvent extraction were compressed into films, then checked the declining of C=O at 1739 cm^{-1} corresponding to acetate groups, with an internal standard peak at 958 cm^{-1} corresponding to C-H bending (out of plane) [8]. Figure 4.2 shows FTIR patterns of pure EVA. The modified EVAs demonstrate hydroxyl groups at wavenumber around 3500 cm^{-1}, as can be seen in Figure 4.3. The absorbance ratio of the modified EVA at each screw speed is shown in Table 4.3. The modified EVA at 10 rpm had the lowest ratio, which represented the lowest remaining of acetate groups along the EVA chains suggesting the highest conversion.
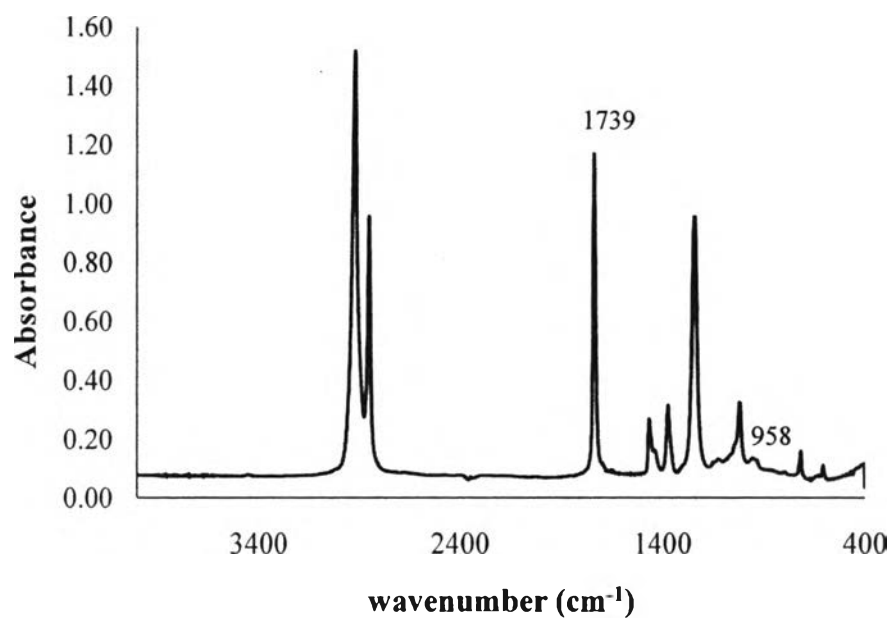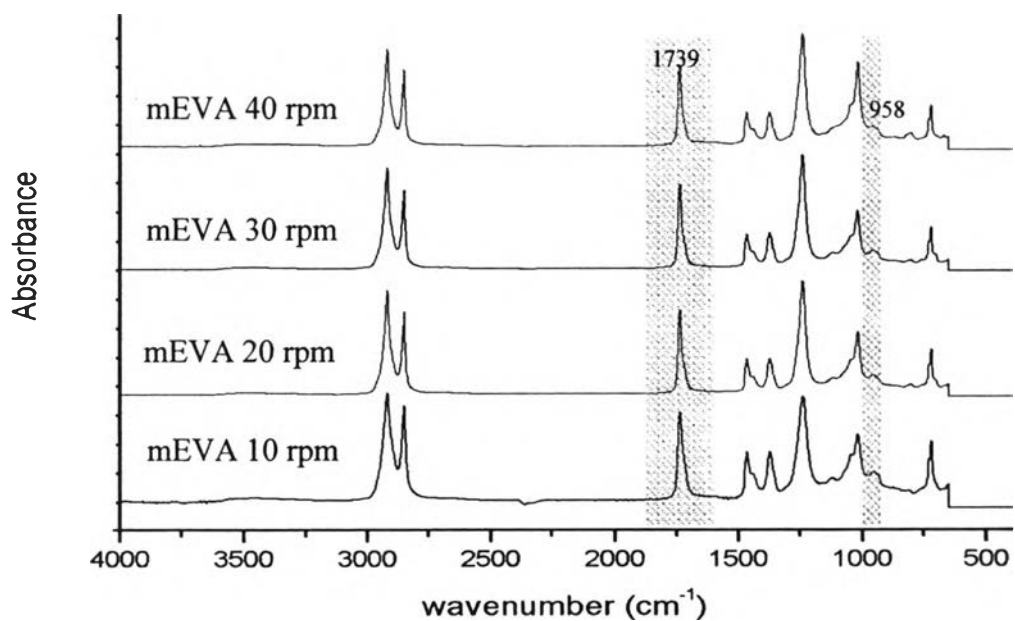
Figure 4.2 FTIR pattern of pure EVA.

Figure 4.3 FTIR pattern of modified EVAs at each screw speed.

Table 4.3 Absorbance ratio of pure EVA and modified EVAs

sample	Absorbance		ratio
	1739 cm^{-1}	958 cm^{-1}	
pure EVA	0.963	0.136	7.08
mEVA 10 rpm	0.800	0.313	2.56
mEVA 20 rpm	0.707	0.190	3.72
mEVA 30 rpm	0.707	0.179	3.94
mEVA 40 rpm	0.675	0.203	3.33

4.4.4 Thermal Properties and Crystallization Behavior

Thermal stability and thermal behavior of the modified EVAs were examined by TGA and DSC, respectively. Figure 4.4 shows thermograms of pure EVA and modified EVAs. Thermal stabilities of the modified EVAs were studied in temperature range of 30-800 °C with heating rate 10 °C/min. The decomposition temperature of each composition is shown in Table 4.4. The first released component was the by-product of the reaction, the second and third components were corresponding to acetate groups and polymer backbone, respectively [9].

Table 4.5 shows transition temperatures from DSC of pure EVA and modified EVAs when being heated from -30 °C to130 °C and cool to -30 °C, then heat again from -30 °C to130 °C with heating rate 5 °C/min. The thermograms are shown in Figure 4.5. Melting temperature and crystallization temperature of modified EVA at higher screw speeds were slightly higher than those of the lower speeds .
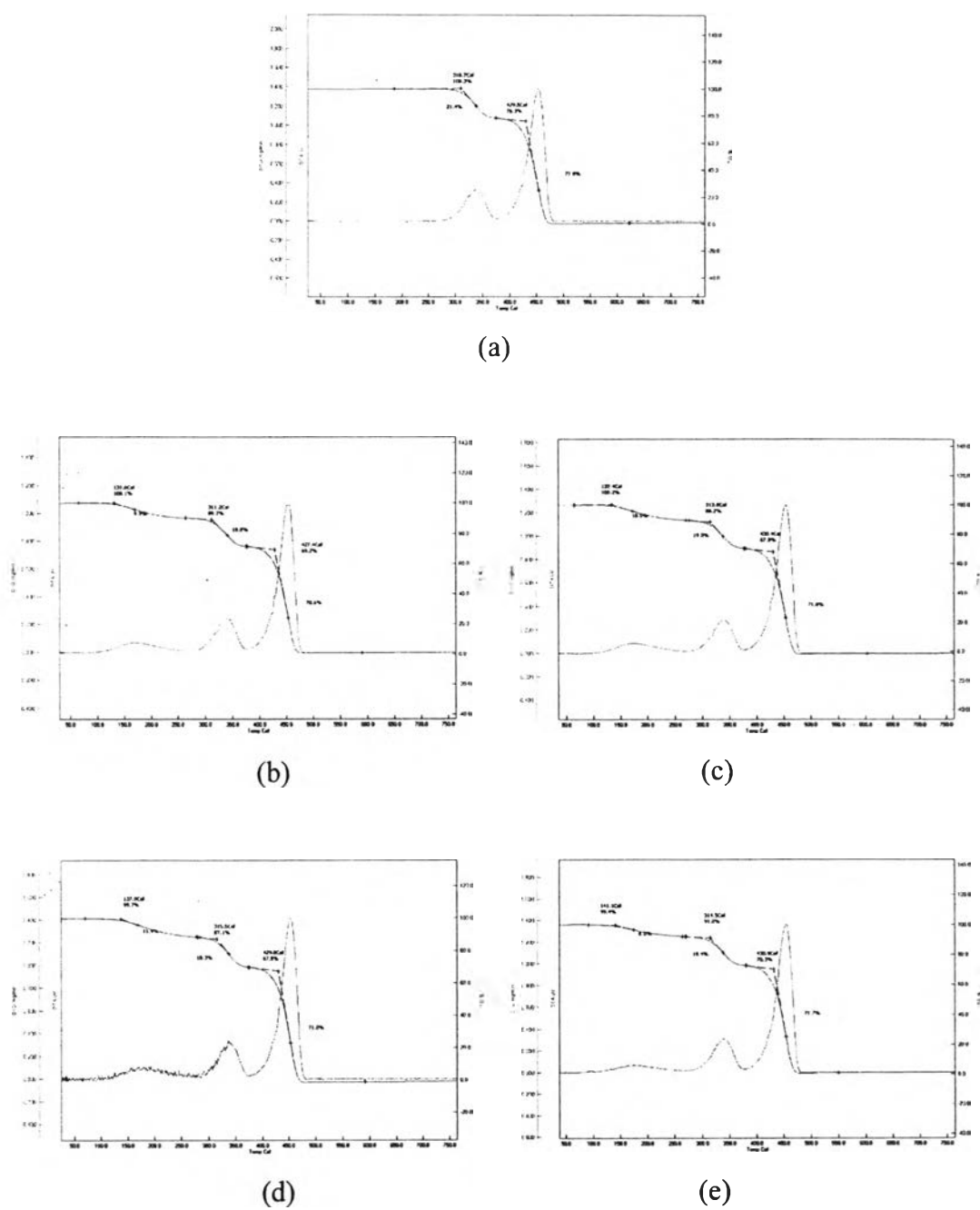
(a)

(b)   (c)

(d)   (e)

Figure 4.4   Thermogravimetric analysis of (a) pure EVA; and modified EVAs various screw speeds of (b) 10 rpm, (c) 20 rpm, (d) 30 rpm, and (e) 40 rpm.

Table 4.4 Decomposition temperature ranges of pure EVA and the modified EVAs at each screw speed

Sample	Mass loss in the temperature range (% wt.)		
	30-325 °C	30-360 °C	360-500 °C
Pure EVA	-	21.4	77.8
mEVA 10 rpm	10.5	19.0	71.0
mEVA 20 rpm	9.9	18.8	70.6
mEVA 30 rpm	11.4	18.3	71.0
mEVA 40 rpm	8.0	19.4	71.7
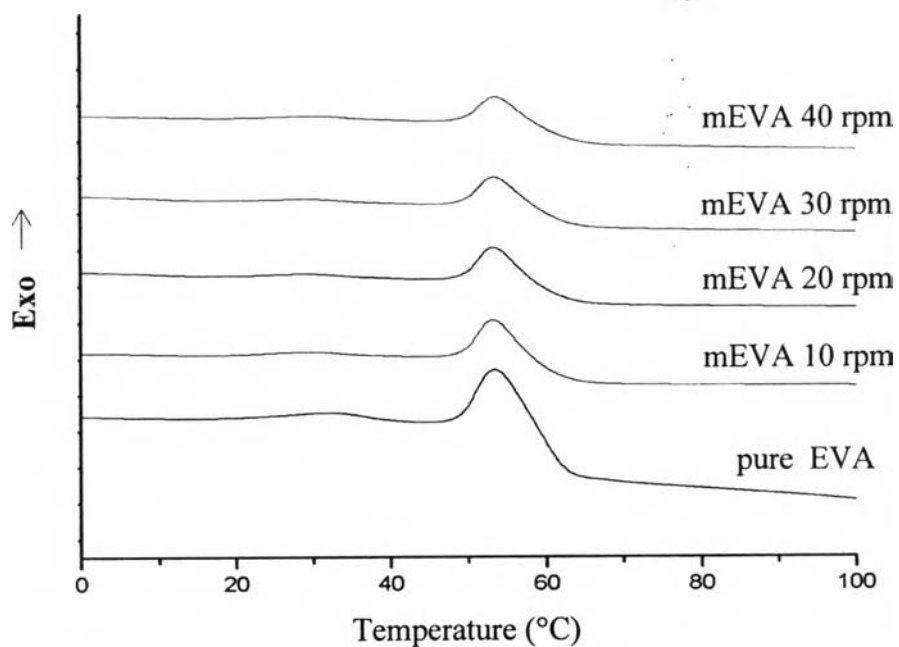
(a)
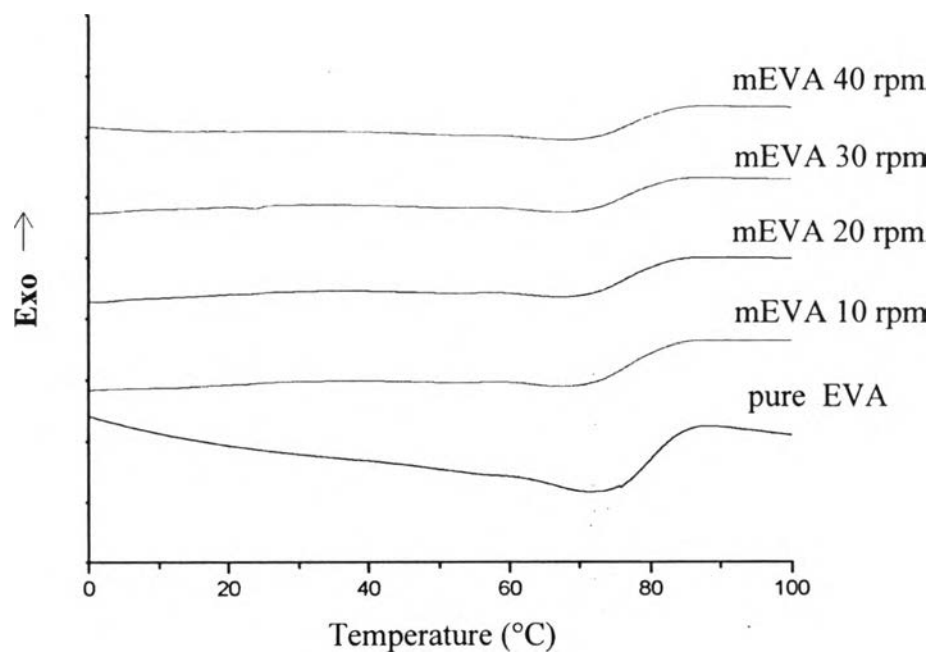
(b)

Figure 4.5 DSC thermogram of pure EVA and modified EVAs (a) exotherm, (b) endotherm (2nd heat).

Table 4.5 T_d, T_m and T_c of pure EVA and the modified EVAs at each screw speed

Sample	Decomposition Temperature			Melting Temperature				Crystallinity (%)		Crystallization Temperature	
	1st	2nd	3rd	1st peak	ΔH (J/g)	2nd peak	ΔH (J/g)	1st peak	2nd peak	1st peak	2nd peak
Pure EVA	-	310.7	429.5	68.84	16.59	-	-	56	-	-	50.71
mEVA 10 rpm	131.6	311.2	427.4	69.80	14.33	125.63	0.44	49	0.2	117.17	52.94
mEVA 20 rpm	133.4	313.8	430.4	70.49	14.49	126.00	0.36	49	0.2	118.01	53.08
mEVA 30 rpm	137.9	315.5	429.8	70.79	16.91	130.12	0.62	58	0.2	117.54	52.77
mEVA 40 rpm	141.1	314.5	430.9	70.48	16.16	130.32	0.71	55	0.2	118.03	53.58

4.4.6 Dynamic Mechanical Properties

The study of dynamic mechanical properties of modified EVA was done by NETZSCH DMA 242, penetration mode from -100 °C to 40 °C. The results are shown in Table 4.6. From Figures (4.6 – 4.8), when comparing with pure EVA, the modified EVAs have lower loss modulus, broader tan δ curves and higher temperature at tan δ peaks or T_g, These confirm the existing of hydrogen bonding along the modified EVA chains [10]. The hydrogen bonding that occurred can constrain the mobility of modified EVA chains.

The lower Tg of the 40 rpm sample than that of pure EVA is due to plasticization effect of unreacted 1-dodecanol. Since the residence time in the extruder was too short for the reaction to occur [11].

Table 4.6 Storage Modulus, Loss Modulus and tan δ of modified EVA at various screw speeds

Screw speed	E'		E''		Tan δ
(rpm)	Onset(°C)	Value(MPa)	Onset(°c)	Value(MPa)	(°C)
Pure EVA	-27.2	13200.1	-17.2	1617	-5.3
mEVA 10 rpm	-30.1	11747.1	-20.9	1292	-2.6
mEVA 20 rpm	-32.6	14305.5	-22.5	1458	-3.3
mEVA 30 rpm	-34.3	15031.9	-22.4	1424	-4.3
mEVA 40 rpm	-31.5	13719.7	-23.2	1563	-7.7

Storage Modulus
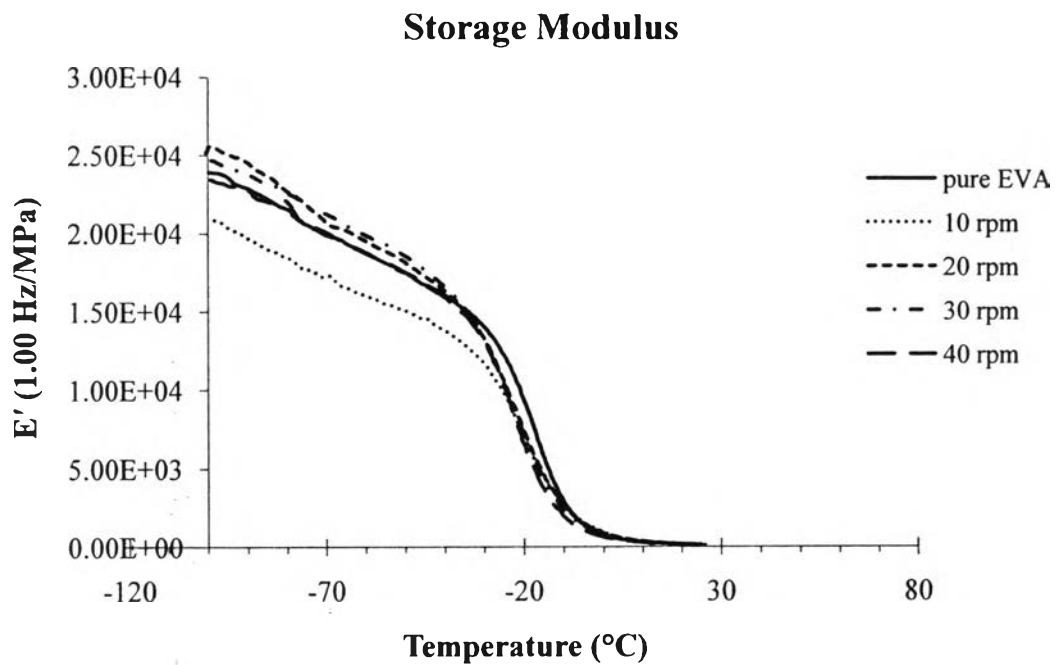

Figure 4.6 Storage Modulus of transesterified EVA at various screw speeds.
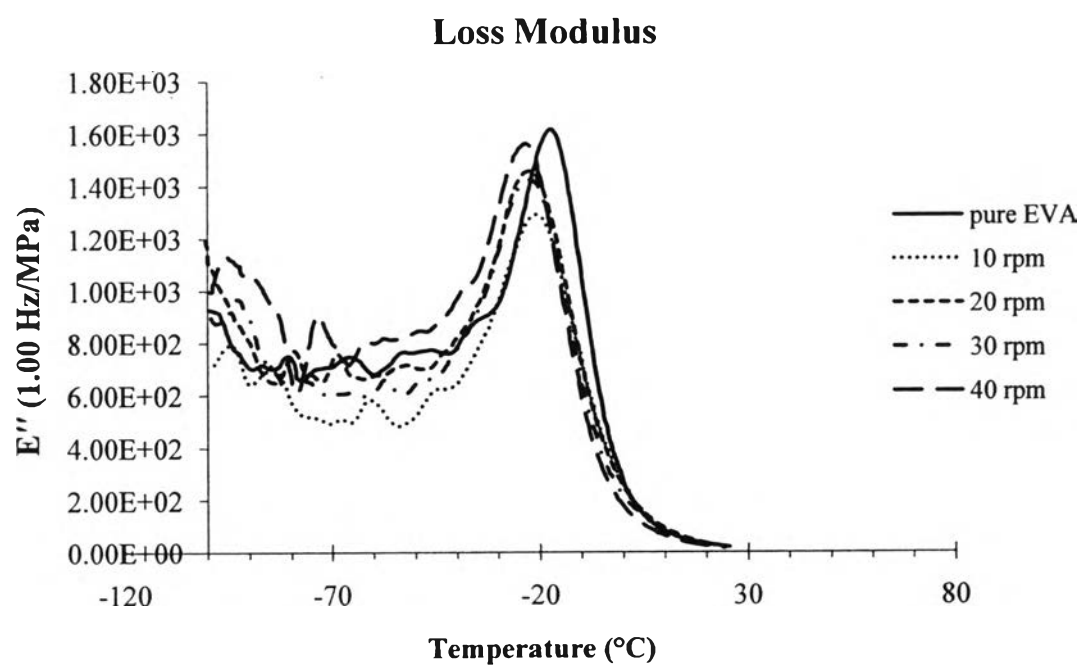
Loss Modulus

Figure 4.7 Loss Modulus of transesterified EVA at various screw speeds.
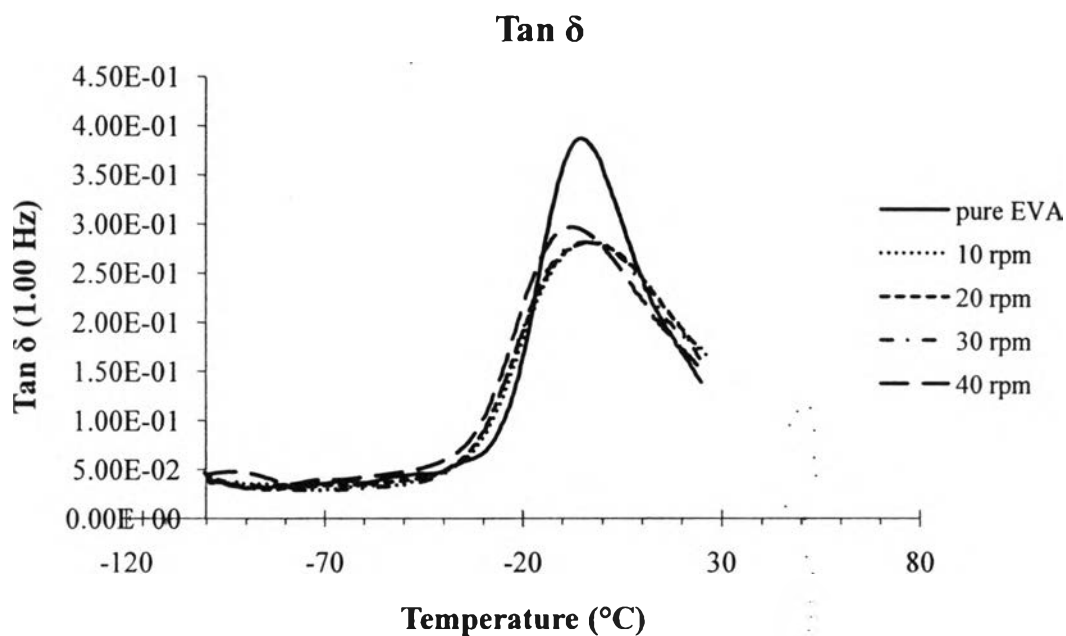
Tan δ

Figure 4.8 Tan δ of transesterified EVA at various screw speeds.

4.5 Conclusions

Transesterification of EVA was done in a twin-screw extruder, which its L/D ratio is 40:1, by 1-dodecanol and DBTDL as a catalyst. The highest conversion was achieved when the reaction occurred at the screw rotating speed of 10 rpm, which can be observed in FTIR and dynamic mechanical test compared with those of pure EVA and another modified EVA. The modified EVA produced at 10 rpm had the lowest existed carbonyl group and lower loss modulus, lower area under tan δ curves, and higher temperature at tan δ peaks or T_g, respectively, where melting temperatures of those modified EVA were slightly higher than pure EVA as a result of intermolecular hydrogen bonding.

4.6 Acknowledgements

4.7 References

[1]   Becquart, F., Taha, M., Zerroukhi, A., Kaczun, J., and Llauro, M.F. (2007) Microstructure and properties of poly(vinyl alcohol-co-vinyl acetate)-g-ε-caprolactone. European Polymer Journal, 43, 1549-1556.

[2]   Jiang, H., He, J., Liu, J., and Yang, Y. (2002) Synthesis and characterization of poly(ethylene-co-vinyl alcohol)-graft-poly(epsilon-caprolactone). Polymer Journal, 34, 682-686.

[3]   Brown, S.B. (1991) Annual Reviews of Material Science, 21, 409-35.

[4]   Janssen, L.P.B.M. (2004). Reactive Extrusion Systems. New York: Marcel Dekker.

[5]   Lambla, M., Druz, J., Bouilloux, A. (2004) Transesterification reactions in molten polymers. Polymer Engineering and Science, 27(16), 1221-1228.

[6]   Vergnes, B., Berzin, F. (2006) Modeling of reactive systems in twin-screw extrusion: challenges and applications. Comptes Rendus Chimie, 9, 1409-1418.

[7]   Kim, P.J., and White, J.L. (1994) Transesterification of ethylene vinyl acetate copolymer in a modular intermeshing twin screw extruder with different screw configurations. Journal of Applied Polymer Science, 54, 33-45.

[8]   Coates, J. (2000). Interpretation of Infrared Spectra, A Practical Approach. Chichester: John Wiley & Sons Ltd.

[9]   Fernández, M.D., and Fernández, M.J. (2008) Thermal decomposition of copolymers from ethylene with some vinyl derivatives. Journal of Thermal Analysis and Calorimetry, 91(2), 447-454.

[10]   Zhu, Y., Wang, B., Gong, W., Kong, L., and Jia, Q. (2006) Investigation of the Hydrogen-Bonding Structure and Miscibility for PU/EP IPN Nanocomposites by PALS. Macromolecules, 39, 9441-9445.

[11]   Zhu, W., Jaluria, Yo. (2004) Residence time and conversion in the extrusion of chemically reactive materials. Polymer Engineering and Science, 41, 1280-1291.