

CHARACTERISATION OF PALM-BASED POLYOLS BY GEL PERMEATION CHROMATOGRAPHY WITH COMBINED DETECTORS

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ABSTRACT

Gel permeation chromatography (GPC) with combined detectors, i.e. differential refractive index (DRI) and viscometer, was used to analyse molecular weight averages of palm-based polyol samples (POP Pioneer 100 and POP Pioneer derivatives, three types of POP Primer and a POP Premier). Elution was carried out using tetrahydrofuran as the mobile phase at 30°C at a flow rate of 1 ml min⁻¹ on a PLgel Mixed D column. Narrow molecular weight distribution (MWD) polystyrene was used as the calibration standard to generate a universal calibration for quantification of the absolute molecular weight (MW) averages and MWD.

POP Pioneer 100 was found to have a number average molecular weight (Mn) ranging from 1861 to 2800 Daltons, a weight-average molecular weight (Mw) of 10 600 to 18 000 Daltons and polydispersity index (PDI) of 5.5 to 6.5 with a broad bimodal MWD. POP Pioneer derivatives had Mn ranging from 2500-2700 Daltons, Mw from 27 110-30 500 Daltons, PDI from 10.2-11.6 and a broad bimodal MWD. POP Premier had Mn from 1290-2215 Daltons, Mw from 17 700-21 500 Daltons and PDI from 7.8-16.7 with broad bimodal MWD. All three types of POP Primer showed close values of MW average with Mn between 1800 and 1900 Daltons, Mw from 7700-7900 Daltons, PDI from 3.8-4.2 and with a skewed bimodal MWD. The Mark-Houwink plots of palm-based polyols showed that the changes in their structures were insignificant over the range of MWD, except for POP Primer Types 2 and 3 where branching was more obvious at the higher end of the molecular weight.

Keywords: gel permeation chromatography, palm-based polyols.

Date received: 24 January 2011; **Sent for revision:** 17 November 2011; **Received in final form:** 23 December 2011; **Accepted:** 21 May 2012.

INTRODUCTION

Gel permeation chromatography (GPC) is a common analytical method for determining the molecular masses and molecular weight distribution of organic and natural polymers (Kovuttikulrangsie and Sakdapipnich, 2004; Wu, 2004; Kadnaim *et al.*, 2005; Mateos *et al.*, 2007). GPC, as compared

with other methods such as osmometry and static light scattering, determines not only average values but also the complete molecular weight distribution (MWD). The molecular weight (MW) of polymer materials covers a large range – from several hundreds (paints, coatings, functionalised polymers) to millions of Daltons. Polymers are usually polydispersed in terms of MW. Because of the kinetics of polymerisation their MW are usually quoted as a series of molecular weight averages, such as the number average (Mn), the weight average (Mw), the viscosity average (Mv), and the z weight average (Mz) molecular weight, and each

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quantity represents one moment of MWD. MWD is the most often used measure of a polymer's MW.

Conventional GPC which uses a single concentration detector, refractive index (RI), is only able to provide 'equivalent' molecular masses compared with the polymer standards used to calibrate the instrument. GPC coupled with triple detection (viscosity, light scattering and RI) or dual detection (viscosity and RI) can be applied for analyses at ambient temperature with a mobile phase, *e.g.* tetrahydrofuran and chloroform, and for aqueous-based eluents. Through the use of viscosity detection, structural changes can be detected from the Mark-Houwink plot or conformation plot. This is a plot of double-logarithmic intrinsic viscosity (IV) *vs.* MW. The Mark-Houwink plot reflects the structural changes such as branching and chain rigidity (Olivier and Walkenhorst, 2002).

This article will discuss the use of the GPC method with combined detectors to characterise palm-based polyols developed by the Advanced Oleochemical Technology Division (AOTD) of the Malaysian Palm Oil Board.

MATERIALS AND METHODS

Materials

POP Pioneer 100, POP Pioneer derivatives, POP Primer Types 1, 2 and 3, and POP Premier were obtained from the Polymer and Composite Group, AOTD. The polystyrene standards (PS) for the PLgel Mixed D column with MW ranging from 580-275 300 Daltons were sourced from Polymer Laboratories, Shropshire, United Kingdom. Each vial contained a pure polystyrene compound with known Mp (molecular peak number) and IV.

Preparation of Polystyrene Standards for GPC Calibration

For the purpose of GPC calibration, a concentration of 2 mg ml⁻¹ of each of the PS standards was prepared by allowing the polymer to dissolve in tetrahydrofuran overnight, and then shaken with a vortex mixer prior to use.

General Preparation of Palm-based Polyols for GPC Analyses

The samples were dissolved in tetrahydrofuran to give an accurate concentration at 2 mg ml⁻¹. Between four and five replicates of the polyol samples were prepared for GPC analyses. The prepared samples were left overnight and analysed the next day.

Gel Permeation Chromatography (GPC)

An integrated GPC system (PL-GPC 50) with combined detectors, comprising differential refractive index (DRI) and viscometer, was used to measure the various MW averages of palm-based polyols. A PL gel 3 μm Mixed D column (Polymer Laboratories, United Kingdom) (300 x 7.5 mm) was used for separation. The mobile phase used was HPLC-grade tetrahydrofuran (Merck), with 5% butylated hydroxyl toluene (BHT) added to prevent column degradation. The experiment was carried out at 30°C at a flow rate of 1 ml min⁻¹. The GPC system was operated using the Cirrus software to generate a universal calibration and to predict the molecular weight averages for the polyol samples.

PS Calibration Standards and Universal Calibration

A series of 10 calibration PS standards were analysed to generate a universal calibration – a plot of log MW multiplied by IV *vs.* retention time. The samples were analysed using the universal calibration to provide data on MW averages, MWD and Mark-Houwink plot.

Hydroxyl Values

Hydroxyl value (OHV) is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample. Acid number (AN) and OHV of the palm-based polyol samples were determined by the AOCS Standard Methods, namely, Cd 3a -63 (2004) and Cd 13-60 (2004), respectively (AOCS, 2004).

RESULTS AND DISCUSSION

POP Pioneer 100 was prepared using refined bleached palm olein (RBPOo). POP Pioneer derivatives were prepared with RBPOo and a vegetable oil (VO) (> 50% unsaturation). POP Primer Types 1, Type 2 and Type 3 were prepared from a blend of RBPOo:VO (< 18% unsaturation) at ratios of 40:60, 80:20 and 90:10, respectively. POP Premier was made primarily of palm kernel olein blended with 10% VO (> 50% unsaturation) as its starting material. The AOTD-formulated polyols followed the route of synthesis where the VO was epoxidised followed by ring opening through alcoholysis (Maznee *et al.*, 2008).

Generally, it was observed that Mn of POP Pioneer 100 was above 1800-2800 Daltons, while Mw was between 10 600 and 18 000 Daltons, PDI (polydispersity index) between 5.5 and 6.5, with a skewed bimodal MWD (Figures 1 and 2). Mn for

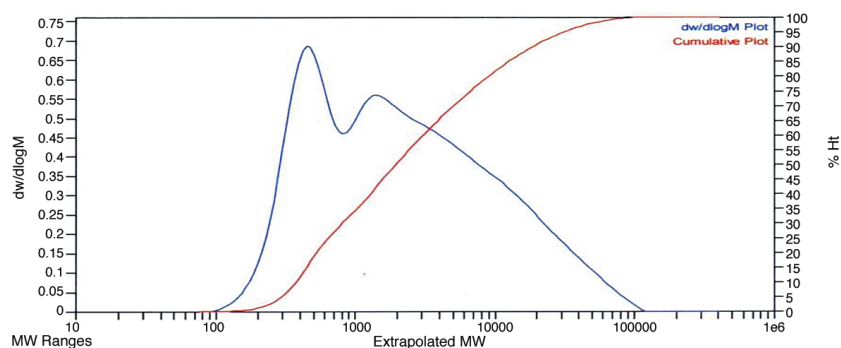


Figure 1. Molecular weight distribution (MWD) plot of POP Pioneer (Batch 1).

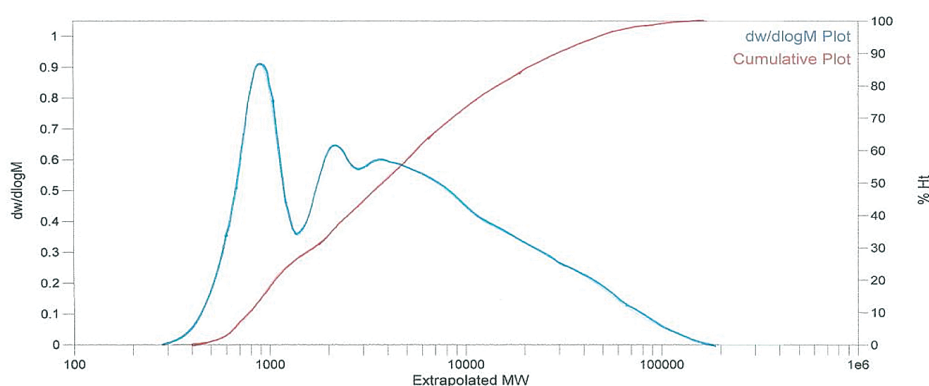


Figure 2. Molecular weight distribution (MWD) plot of POP Pioneer (Batch 2).

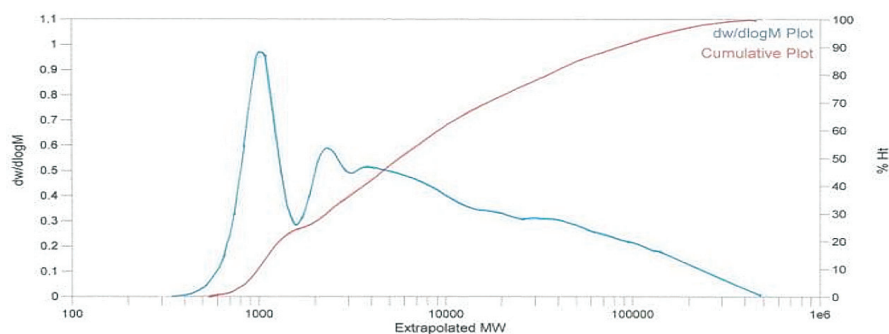


Figure 3. Molecular weight distribution (MWD) plot of POP Pioneer derivatives (Batch 1).

commercially produced RBD palm oil, palm olein and RBD palm superolein-based polyols from Cargill Incorporated had been reported to be lower, ranging from 1406 to 1944 Daltons (de Genova *et al.*, 2008).

POP Pioneer derivatives had similar M_n to POP Pioneer 100 but M_w was twice as high and PDI was more than 10. MWD for both types of POP Pioneer derivatives were skewed bimodally and was quite similar to POP Pioneer 100 but broader (Figure 3). POP Pioneer derivatives were characterised by high PDI and broad bimodal MWD, indicating that they had highly polydispersed systems, and this was attributed to the blend of 10% highly functional unsaturated moiety with RBPOo.

POP Premier was synthesised primarily from palm kernel oil and was expected to have lower molecular weights than palm olein-derived polyols.

However, POP Premier was found to have high M_w (17 000–21 000 Daltons) similar to M_w of POP Pioneer 100. Similar to POP Pioneer derivatives, the high M_w observed for POP Premier can be attributed to the presence of the 10% high functionality unsaturated moiety. MWD of POP Premier was broad with a bimodal pattern, suggesting a highly polydispersed system (Figure 4). The PDI values for three different batches ranged from 7.8 to 16.7, indicating a more polydispersed system than POP Pioneer 100.

The three POP Primer types showed almost similar molecular weight averages and PDI although the ratios of the blended starting material varied. MWD for POP Primer Types 1, 2 and 3 were mostly skewed bimodally (Figures 5 to 7). Unlike POP pioneer derivatives, the POP Primer types did not have broad MWD as POP Pioneer derivatives,

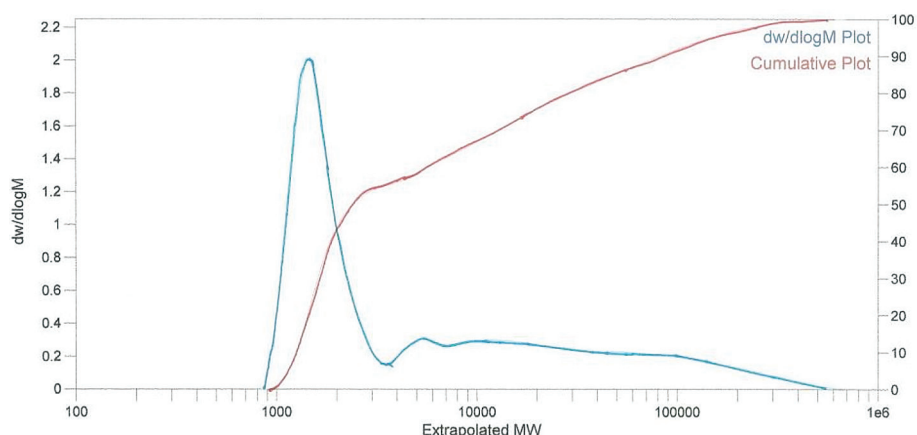


Figure 4. Molecular weight distribution (MWD) plot of POP Premier.

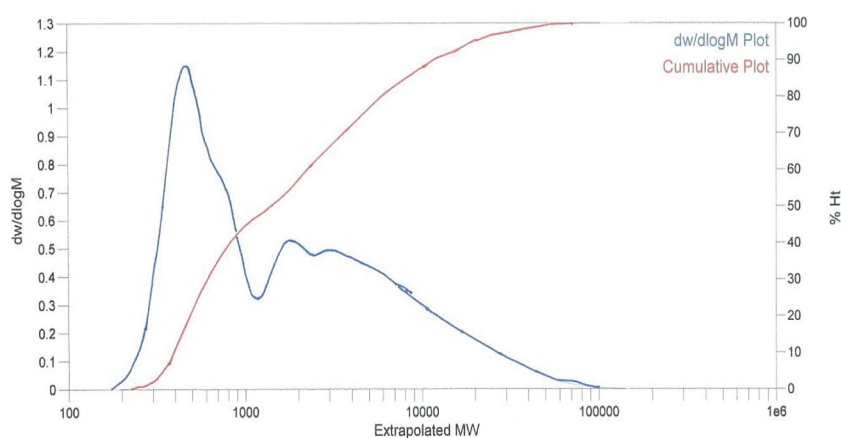


Figure 5. Molecular weight distribution (MWD) plot of POP Primer Type 1.

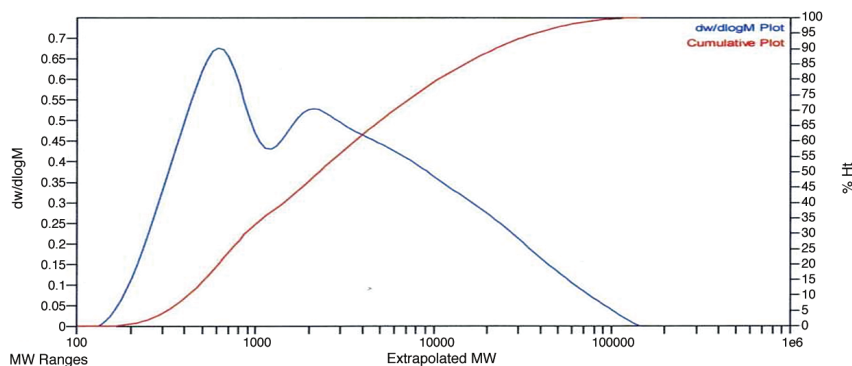


Figure 6. Molecular weight distribution (MWD) plot of POP Primer Type 2.

suggesting that they were less polydispersed. The low unsaturated component in POP Primer did not interact like the highly unsaturated component in POP Pioneer derivatives explained previously. OHV (Table 1) decreased in the order of POP Pioneer derivatives > POP Primer Type 3 > POP Primer Type 2 > POP Primer Type 1. This was because as the low unsaturated moiety portion increased, less hydroxyl groups were formed, and also explained the lower Mw for all three types of POP Primer as compared with POP Pioneer derivatives.

Mark-Houwink Constants and Plot

GPC separation is based on the effective molecular size of a polymer in a dilute solution. The polymer size is a result of interactions of chain segments with the surrounding solvent in a dilute solution. Polymer molecules are represented as equivalent hydrodynamic spheres. The hydrodynamic volume of a polymer molecule is a function of its IV, and its MW is expressed by the Mark Houwink (M-H) equation: $[\eta] = KM\alpha$,

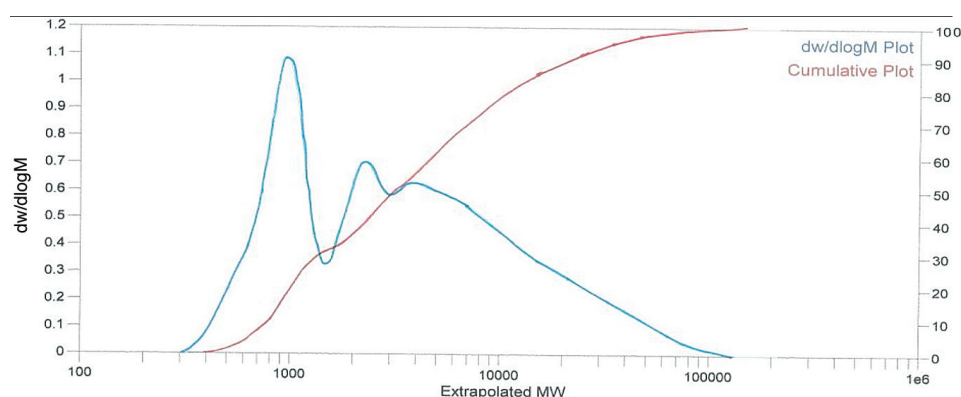


Figure 7. Molecular weight distribution (MWD) plot of POP Primer Type 3.

TABLE 1. MOLECULAR WEIGHT AVERAGE AND HYDROXYL VALUE CHARACTERISTICS OF PALM-BASED POLYOLS

Polyol	OHV (mg KOH g ⁻¹ of sample)	Mp ± SD (CV)	Mn ± SD (CV)	Mv ± SD (CV)	Mw ± SD (CV)	PDI ± SD (CV)	K	α
POP Pioneer 100 (Batch 1)	139	1 161 ± 60 (5.2%)	2 769 ± 90 (3.2%)	7 616 ± 333 (4.4%)	18 016 ± 1704 (9.5%)	6.5 ± 0.4 (6.2%)	1 144	0.233
POP Pioneer 100 (Batch 2)	143	1 193 ± 49 (4.1%)	2 820 ± 117 (4.1%)	7 744 ± 353 (4.6%)	18 341 ± 1430 (7.8%)	6.5 ± 0.4 (6.2%)	1 170	0.21
POP Pioneer 100 (Batch 3)	111	1 061 ± 79 (7.4%)	2 609 ± 188 (7.2%)	6 995 ± 497 (7.1%)	14 200 ± 765 (5.4%)	5.5 ± 0.4 (7.3%)	790	0.242
POP Pioneer 100 (Batch 4)	120	770 ± 37 (4.8%)	1 861 ± 148 (8.0%)	4 695 ± 228 (4.9%)	10 622 ± 440 (4.1%)	5.7 ± 0.3 (5.3%)	1 152	0.240
POP Pioneer derivatives (9:1) (Batch 1)	182	977 ± 83 (8.5%)	2 554 ± 240 (9.4%)	1 0887 ± 970 (8.9%)	28 953 ± 1932 (6.7%)	11.6 ± 0.8 (6.8%)	878	0.238
POP Pioneer derivatives (9:1) (Batch 2)	180	1 050 ± 46 (4.4%)	2 783 ± 139 (5.0%)	1 1216 ± 728 (6.5%)	30 549 ± 2925 (9.6%)	10.9 ± 0.71 (6.5%)	824	0.258
POP Pioneer derivatives (9:1) (Batch 3)	146	1 027 ± 75 (7.3%)	2 675 ± 171 (6.4%)	10 037 ± 610 (6.1%)	27 117 ± 787 (2.9%)	10.2 ± 0.4 (3.9%)	823	0.270
POP Primer Type 1	89	1 075 ± 64 (6.0%)	1 972 ± 119 (6.0%)	4 465 ± 364 (8.2%)	7 765 ± 472 (6.1%)	3.8 ± 0.2 (5.3%)	547	0.283
POP Primer Type 2	103.3	1 086 ± 111 (10.2%)	1 954 ± 270 (13.8%)	4 475 ± 416 (9.3%)	7 915 ± 330 (4.2%)	4.1 ± 0.5 (12.2%)	696	0.245
POP Primer Type 3	144	959 ± 86 (9.0%)	1 844 ± 158 (8.6%)	4 214 ± 295 (7.0%)	7 769 ± 181 (2.3%)	4.2 ± 0.3 (7.1%)	678	0.286
POP Premier (Batch 1)	65.7	1 527 ± 119 (7.8%)	2 215 ± 209 (9.4%)	7 222 ± 778 (10.8%)	17 745 ± 1648 (9.3%)	7.8 ± 0.7 (9.0%)	238	0.386
POP Premier (Batch 2)	69.2	824 ± 27 (3.3%)	1 290 ± 34 (2.6%)	4 749 ± 246 (5.2%)	21 517 ± 1239 (5.8%)	16.7 ± 0.6 (3.6%)	301	0.344
POP Premier (Batch 3)	70.5	1 040 ± 82 (7.9%)	1 716 ± 188 (11.0%)	5 776 ± 620 (10.7%)	18 109 ± 932 (5.1%)	10.6 ± 1.2 (11.3%)	285	0.314

Note: SD: standard deviation.

CV: coefficient of variation.

OHV: hydroxyl value.

Mp: peak average molecular weight.

Mv: viscosity average molecular weight.

Mn: number average molecular weight.

Mw: weight average molecular weight.

PDI: polydispersity index.

K and α: Mark-Houwink constants.

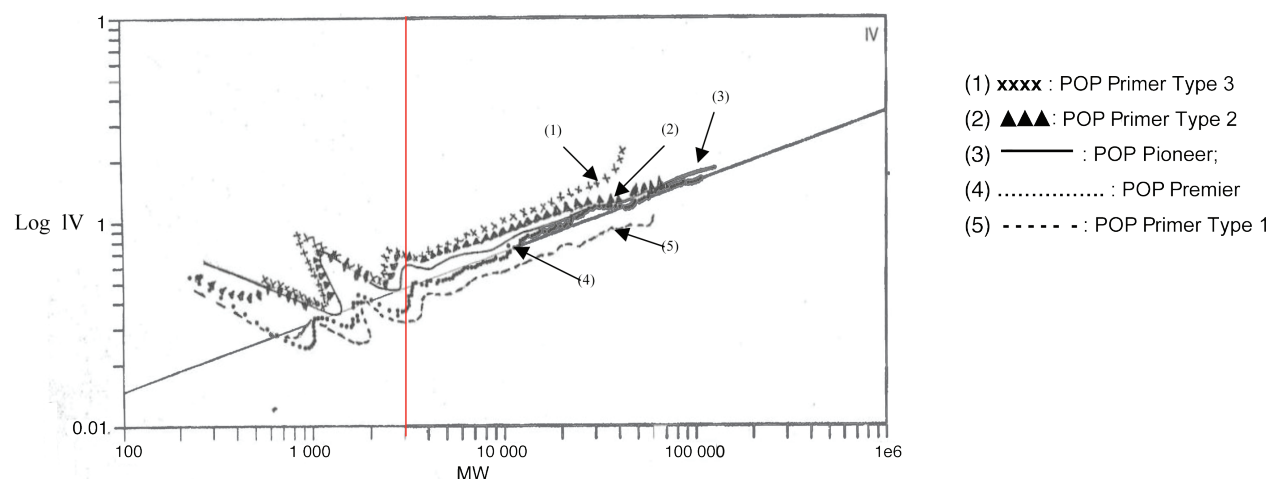


Figure 8. Overlay of Mark-Houwink plots for Advanced Oleochemical Technology Division's palm-based polyols.

where K and α are the M-H constant and exponent, respectively, for the polymer under a specific experimental condition (solvent, temperature, etc.). The values of α for POP Pioneer, POP Pioneer derivatives and POP Primer Types 1, 2 and 3 were similar, ranging from 0.24-0.29. However, POP Premier showed a higher α value, at greater than 0.3. POP Premier comprised palm kernel olein as the major starting material; thus, this may explain the different α values compared with those of the palm olein-based polyols.

The M-H plot derived from the log-log plot of IV vs. MW was used to elucidate the structural information of the polyols. The M-H plot reflects structural changes such as branching and chain rigidity. The slope of the plot indicates the compactness of the molecular structure (Olivier and Walkenhorst, 2002). Figure 8 shows the overlay of M-H plots for the palm-based polyols. Structural analyses of the M-H plot start from the right hand side of the red line where the data points are dense showing polymers with high Mw. The plots of POP Pioneer, POP Premier and POP Primer Type 1 show that their slopes were quite consistent, and that their structural changes were not significant across MWD. However, there were significant changes from less branched structures at lower molecular weights to more branched structures at higher molecular weights for POP Primer Type 2 and Type 3. Although the compositions of POP Primer Type 2 and Type 3 were almost similar, their structures were different at the higher end of the MW. Comparison of the slopes of POP Pioneer, POP Primer Type 2 and POP Premier show that their structures were similar at the higher MW portion, as indicated by the close proximity of the slopes.

CONCLUSION

Generally, palm olein-based polyols, e.g. POP Pioneer 100 and POP Pioneer derivatives, were typified by high MW (above 10 000 Daltons) and PDI above 5, with broad bimodal MWD. POP Pioneer derivatives had higher Mw than POP Pioneer, and this can be attributed to the presence of the 10% highly unsaturated moiety used in the starting material. Although POP Premier comprised 90% of palm kernel olein (lower molecular weight than palm olein), it was found to have high Mw (> 18 000 Daltons), and it is highly polydispersed as indicated by a PDI above 7. This could be due to the 10% highly unsaturated moiety used which allowed more hydroxyl groups to be formed. All three types of POP Primer showed lower MW compared with POP Pioneer and POP Pioneer derivatives. POP primer was prepared from varying the ratios of the unsaturated component blended with palm olein, but all of them showed similar Mn, Mw and PDI.

ACKNOWLEDGEMENT

The author would like to thank the Director-General of MPOB for permission to publish this article, and the staff and research officers of the Polymer and Composite Group, and the Process Engineering and Design Unit for providing the palm-based polyols samples.

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