CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of Flexible PVC cable compounds

In any flexible PVC compounds, the most important physical property is softness or hardness, since this determines the physical characteristics of the finished article. Hardness is therefore the main factors taken into account when considering the use of plasticizer. In this experiment typical cable compound formulation with hardness 80A containing different ratios of DOP and chlorinated paraffin has been studied.

The basic formulations for sample preparation are as followed:

Materials	Content (phr)
PVC (K 66)	100
Lead stabilizer	3
Calcium carbonate	30
DOP	50 - 0
Chlorinated paraffin	0 – 50

By using I.C.I. company data[20] as shown in Figure 4.1, it is found that PVC compounds, which have hardness 80A, can be obtained by blending between DOP and chlorinated paraffin at the ratio of 46:5, 42:10, 39:15 and 36:20 respectively.

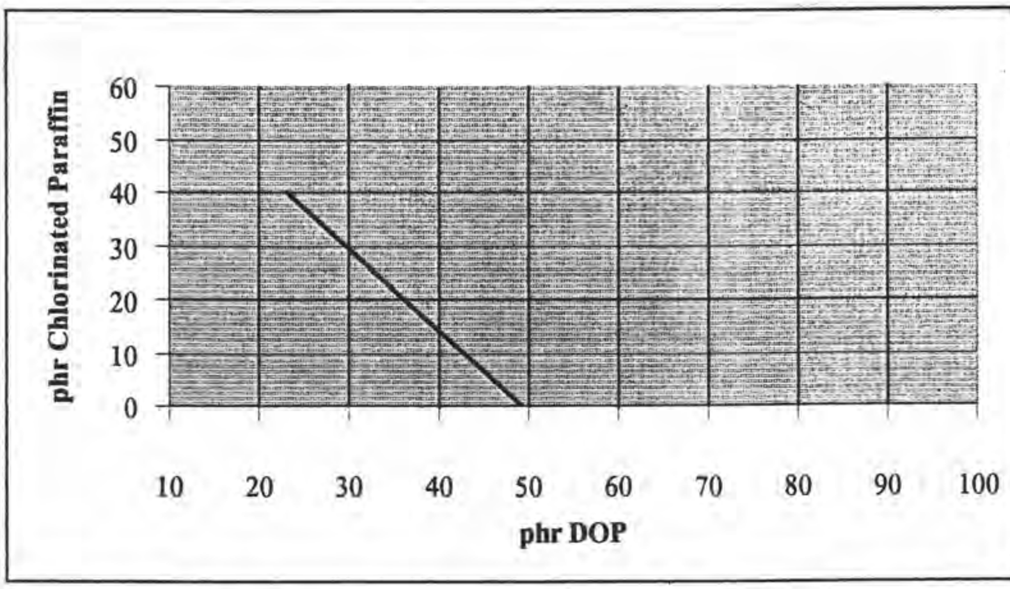

Figure 4.1: Plot of different ratios of DOP and Chlorinated Paraffin for Flexible PVC compound with hardness 80A[20].

After mixing all raw materials following basic formulation: PVC 100 phr, lead stabilizer 3 phr, calcium carbonate 30 phr and using plasticizer blend between DOP and chlorinated paraffin in the ratio that was mentioned in the previous paragraph. The hardness of each PVC compounds was measured but none of these ratios gave hardness 80A as the experiment No. 1, 4, 6 and 8 as shown in Table 4.1.

In order to obtain hardness 80A, by fixing the amount of chlorinated paraffin at 5, 10, 15 and 20 phr, the ratio of DOP has to be adjusted. From Table 4.1 it could be seen that experiment No. 3, 5, 7 and 10 gave PVC compound at hardness 80A which are name as Formulations 2, 3, 4 and 5 respectively (see Table 4.2).

Table 4.1: Hardness of flexible PVC compounds with plasticizer blends of DOP and chlorinated paraffin (CP)

Experiment No.	CP (phr)	DOP (phr)	Hardness
1	5	46	78.4 A
2	5	47	77.9 A
3	5	45	80.8 A
4	10	42	81.8 A
5	10	43	80.9 A
6	15	39	81.5 A
7	15	40	80.6 A
8	20	36	78.4 A
9	20	37	78.1 A
10	20	35	80.6 A

In this study six PVC compound formulations are prepared as shown in Table 4.2. The hardness of the PVC compound of Formulations 1 to 5 is fixed. Formulation 1 is basic formulation which contained only 50 phr of DOP plasticizer. Formulations 2, 3, 4 and 5 are varied the ratios of DOP and chlorinated paraffin to obtained hardness 80A. Formulation 6 contained the same amount of plasticizer but changing from DOP to chlorinated paraffin in order to observe the effect of different type of plasticizer.

Table 4.2: Hardness of six formulations of flexible PVC cable compounds

Materials	Formulation (phr)*					
	1	2	3	4	5	6
PVC (K 66)	100.0	100.0	100.0	100.0	100.0	100.0
$CaCO_3$	30.0	30.0	30.0	30.0	30.0	30.0
Lead stabilizer	3.0	3.0	3.0	3.0	3.0	3.0
Phthalate (DOP)	50.0	45.0	43.0	40.0	35.0	0.0
Chlorinated paraffin	0.0	5.0	10.0	15.0	20.0	50.0
Hardness (Shore A)	80.5	80.8	80.9	80.6	80.6	91.1

Note: *phr is parts per hundred resin.

4.2 Effect of Oil Ageing time on migration of plasticizer blends

The experiments were performed according to JIS K-6301 (Oil resistance test of PVC samples) to determine the percentages of weight loss after immersion in Oils at 70°C for 4 hours. In addition the immersion time was varied from 2 to 4, 24 and 48 hours respectively to observe the effect of oil ageing time on migration of plasticizer blends.

Three specimens of each formulation were weighed to 4 decimal points accuracy and measured the hardness before and after immersed into 4 types of oils, i.e., low and high viscosity motor oil and silicone oil in order to determine the less migration formulation.

Figure 4.2 showed the plot of immersion times and percentages of weight loss of PVC compounds at 70°C for 2, 4, 24 and 48 hours in low viscosity motor oil. Details are shown in Table 1A to 5A (see Appendix A).

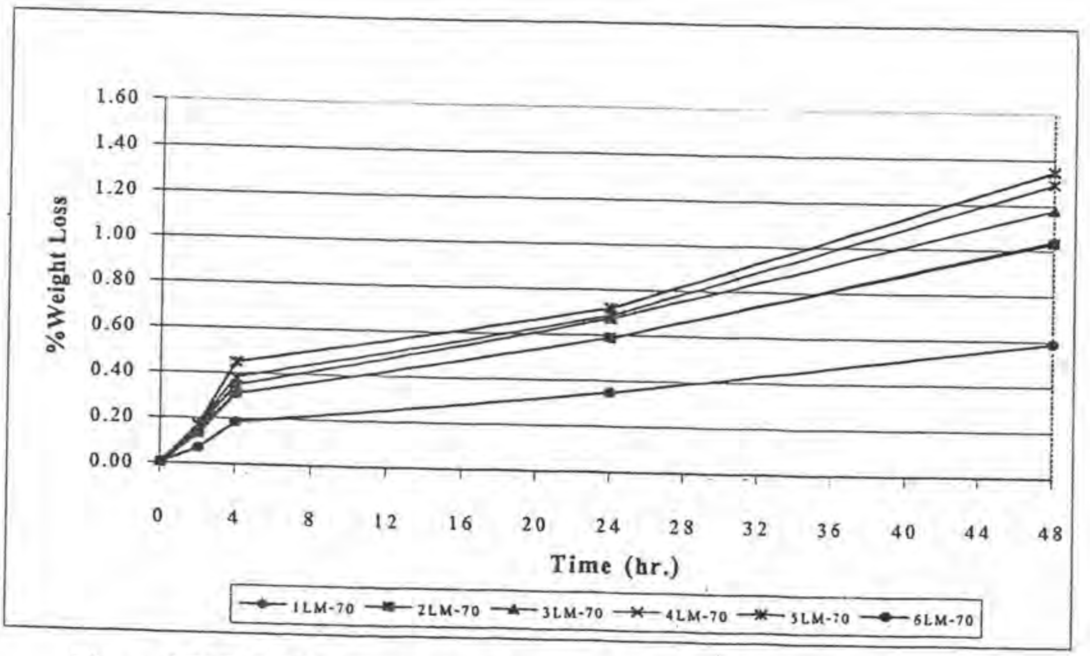

Figure 4.2: Plot of percentages of weight loss of PVC compounds versus immersion times in low viscosity motor oil at 70°C.

It could be observed that migration of plasticizers is increased with increasing time and the rate of migration is increased faster from 0 to 4 hours than 4 to 48 hours. As described by Papaspyrides, C. D., et al[9], plasticizers at the PVC compound surface can migrate into oil medium easier than the remaining plasticizers. Since after this, the van der Waals forces between the PVC chains brought PVC chains closer, making it is more difficult for the remaining plasticizers to migrate out.

As shown in Figure 4.2, Formulation 5 has the highest percentages of plasticizers migration and following by Formulation 4, 3, 1, 2 and 6 respectively. Since Formulation 6 has hardness 90A, containing only chlorinated paraffin plasticizer, which is higher than the other five Formulations which have hardness 80A. Hence its van der Waal force between each PVC chains is stronger than the other formulations. It is more difficult for chlorinated paraffin to migrate out. Comparing Formulation 2 to 5, which has the same hardness, it is found that the higher amount of chlorinated paraffin, the higher percentages of plasticizers migration. Formulation 1, which has only pure DOP, has higher percentages of migration than Formulation 2 which has plasticizer blends.

From these data, it can be concluded that chlorinated paraffin is less compatible to PVC than DOP. Since chlorinated paraffin not only has higher molecular weight than DOP but also contains no hydrogen bonding to interact with PVC. Therefore, it can not use only chlorinated paraffin to plasticized PVC with good properties but it can use a part of chlorinated paraffin with other plasticizers such as DOP. From this study Formulation 2 gave both the less percentages of plasticizers migration and cost effectiveness.

The oil ageing tests are also studied in various oils as shown in Figure 4.3 (high viscosity motor oil), Figure 4.4 (low viscosity silicone oil) and Figure 4.5 (high viscosity silicone oil) which are plotted from data of Table 6A to 20A (see Appendix A) respectively. The results are similar to migration of plasticizers in low viscosity motor oil as followed:

1) Migration of plasticizers is increased with increasing time.
2) Faster migration can be seen in the earlier step of oil Ageing.
3) Chlorinated paraffin can be migrated into oil mediums easier than DOP.
4) The descend-order tendency of plasticizers migration in six formulations is Formulation 6, 2, 1, 3, 4 and 5 respectively.

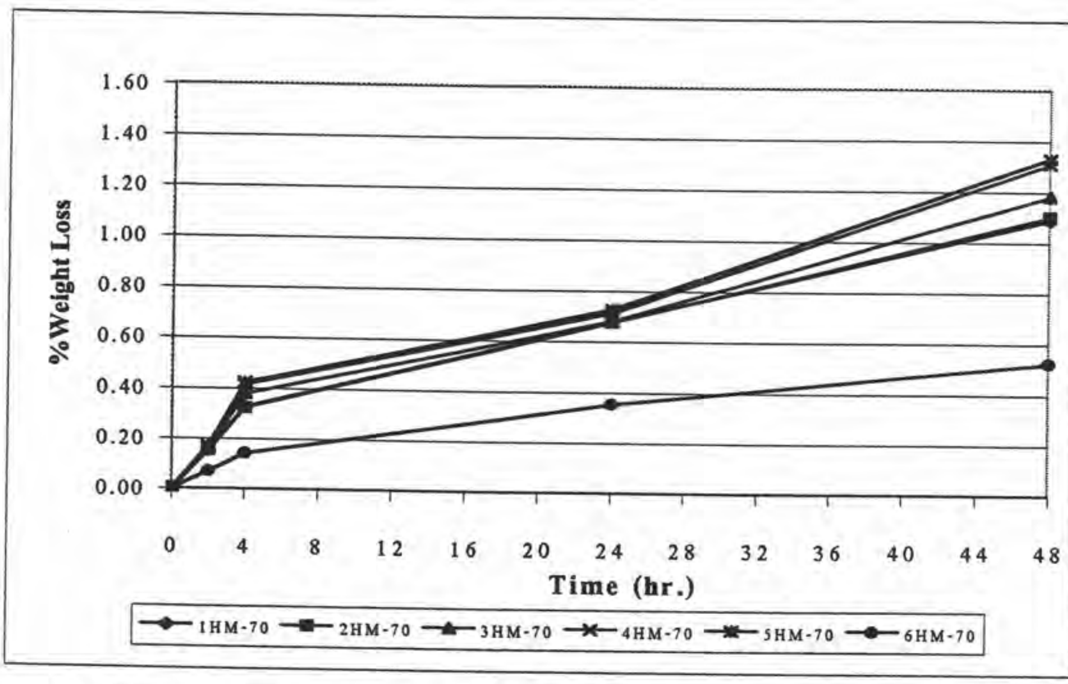

Figure 4.3: Plot of percentages of weight loss of PVC compounds versus immersion times in high viscosity motor oil at 70°C.

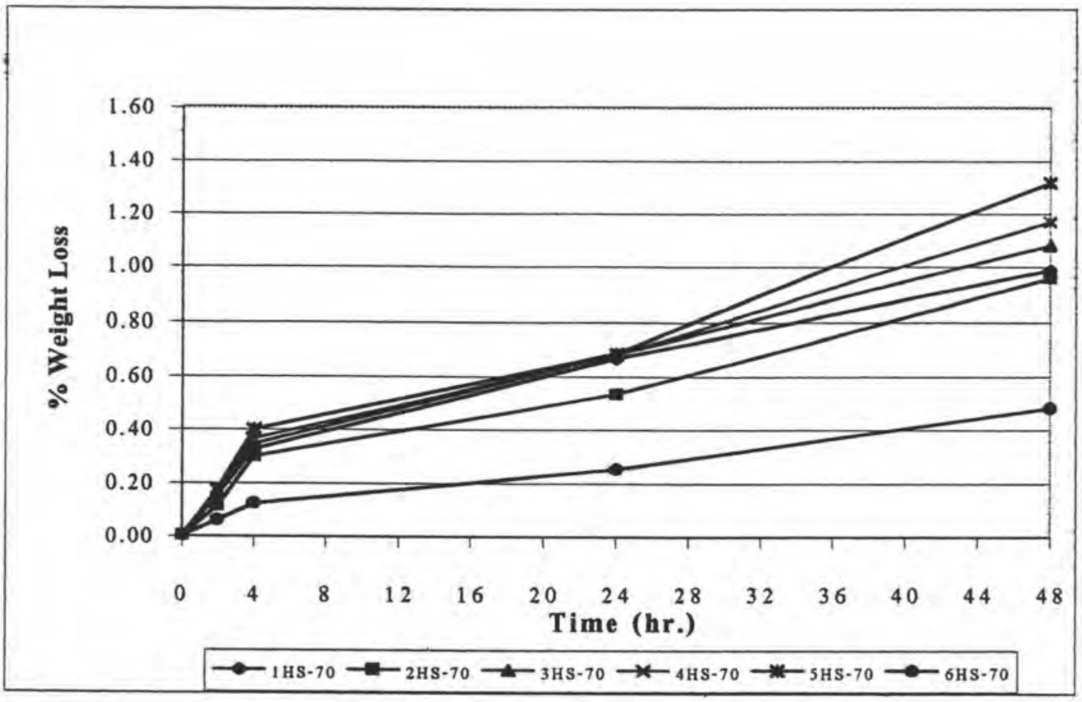

Figure 4.4: Plot of percentages of weight loss of PVC compounds versus immersion times in low viscosity silicone oil at 70°C.

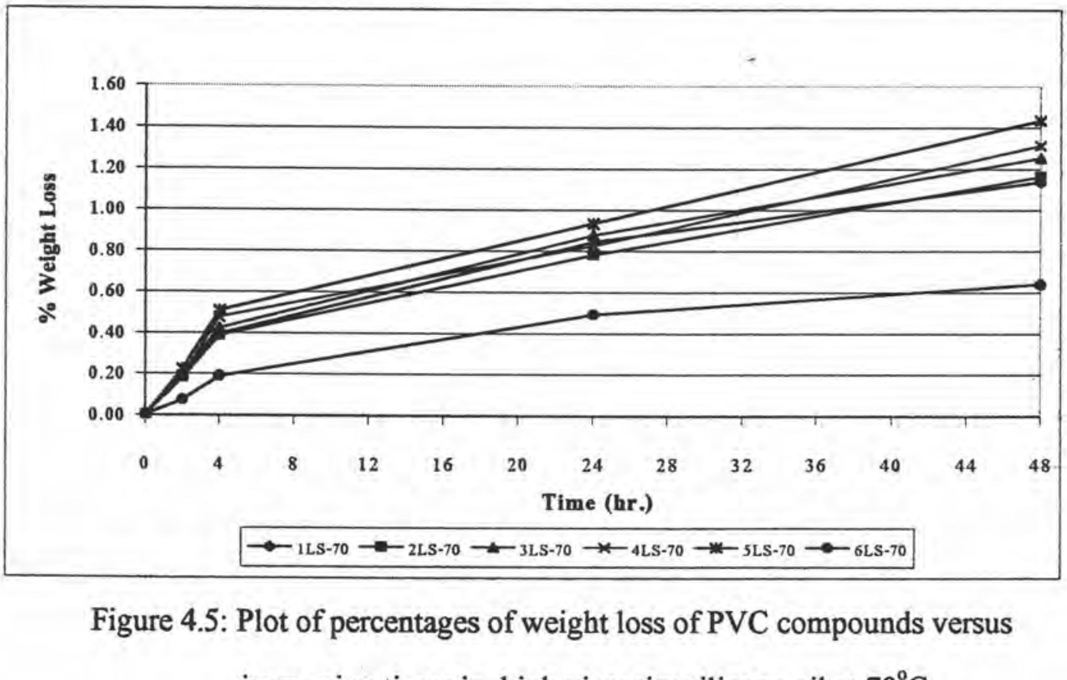

Figure 4.5: Plot of percentages of weight loss of PVC compounds versus immersion times in high viscosity silicone oil at 70°C.

4.3 Effect of Oil Ageing temperature on migration of plasticizer blends

Typical laboratory method of measuring plasticizer migration is oil ageing at 70°C for 4 hours. In this experiment we studied oil ageing at 120 °C to see the effect of plasticizer migration at elevated temperature.

Figure 4.6 showed the plotted of immersion times and percentages of weight loss of PVC compounds at 120 °C for 2, 4, 24 and 48 hours in low viscosity Motor oil. Details are shown in Table 1B to 5B (see Appendix B).

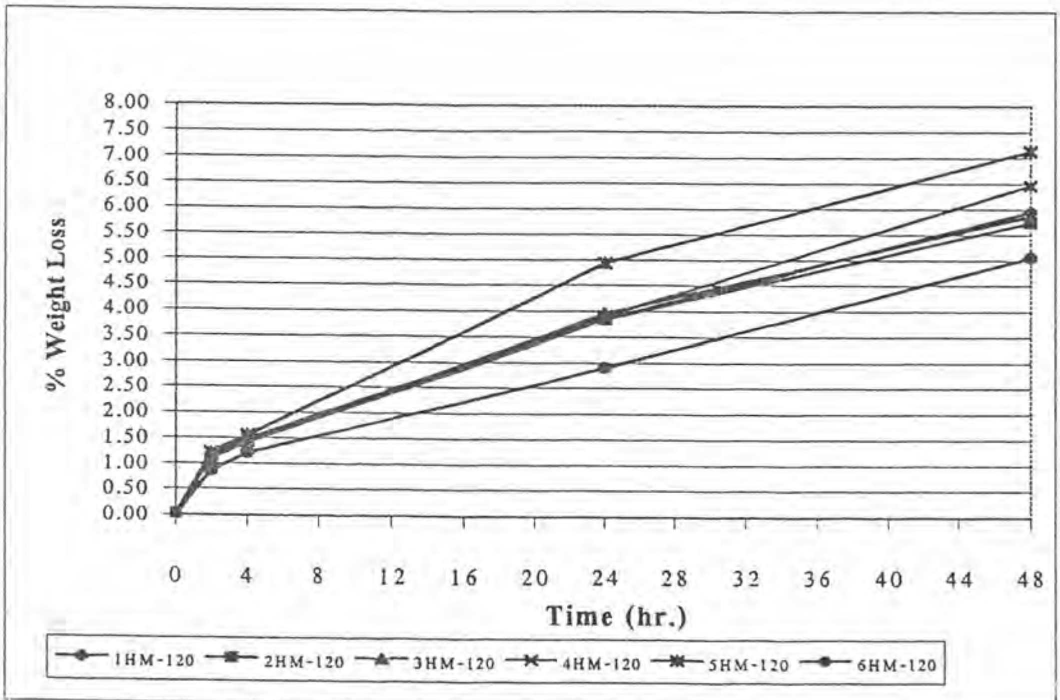

Figure 4.6: Plot of percentage of weight loss of PVC compounds versus immersion times in low viscosity motor oil at 120°C.

It could be observed that migration of plasticizers is similar to migration of plasticizers in low viscosity motor oil at 70°C as followed:

1) Migration of plasticizers is increased with increasing time.

2) Faster migration can be seen in the earlier step of migration time.

3) Chlorinated paraffin can migrated into oil mediums easier than DOP.

4) The descend-order tendency of plasticizers migration in six formulations is Formulation 6, 2, 1, 3, 4 and 5 respectively.

The oil ageing tests are also studied in various oils as shown in Figure 4.7 (high viscosity motor oil), Figure 4.8 (low viscosity silicone oil) and Figure 4.9 (high viscosity silicone oil) which are plotted from data of Table 6B to 20B (see Appendix B) respectively. The results are similar to migration of plasticizers in low viscosity motor oil.

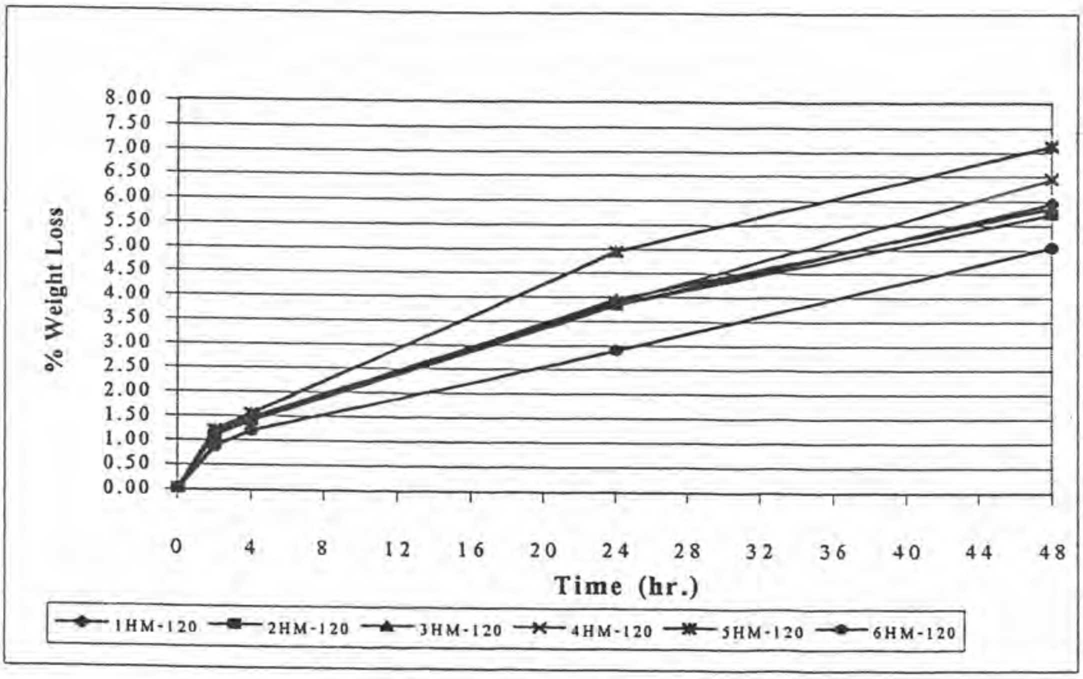

Figure 4.7: Plot of percentages of weight loss of PVC compounds versus immersion times in high viscosity motor oil at 120°C.

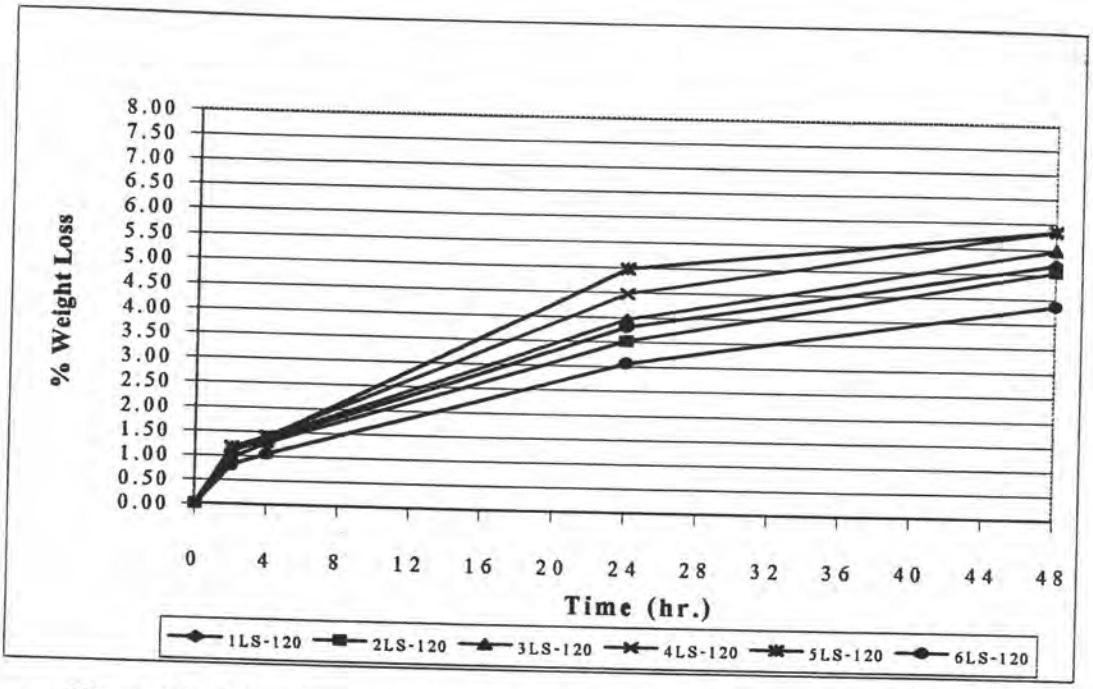

Figure 4.8: Plot of percentages of weight loss of PVC compounds versus immersion times in low viscosity silicone oil at 120°C.

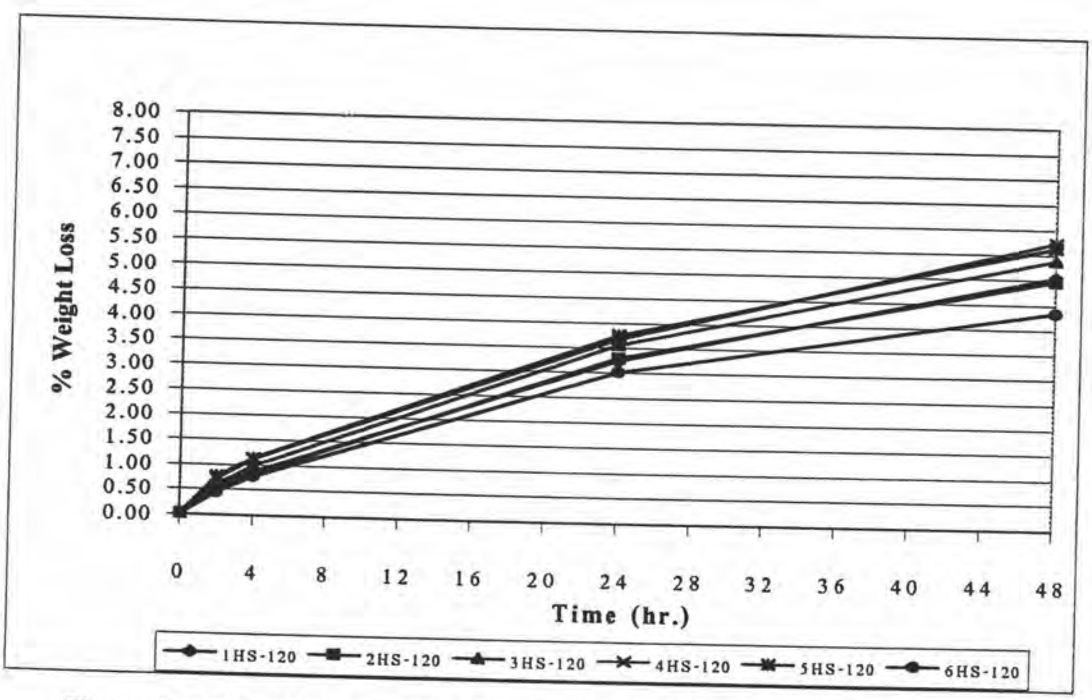

Figure 4.9: Plot of percentages of weight loss of PVC compounds versus immersion times in high viscosity silicone oil at 120°C.

Figure 4.10 showed the oil ageing tests of PVC compounds at 70°C and 120°C in low viscosity motor oil.

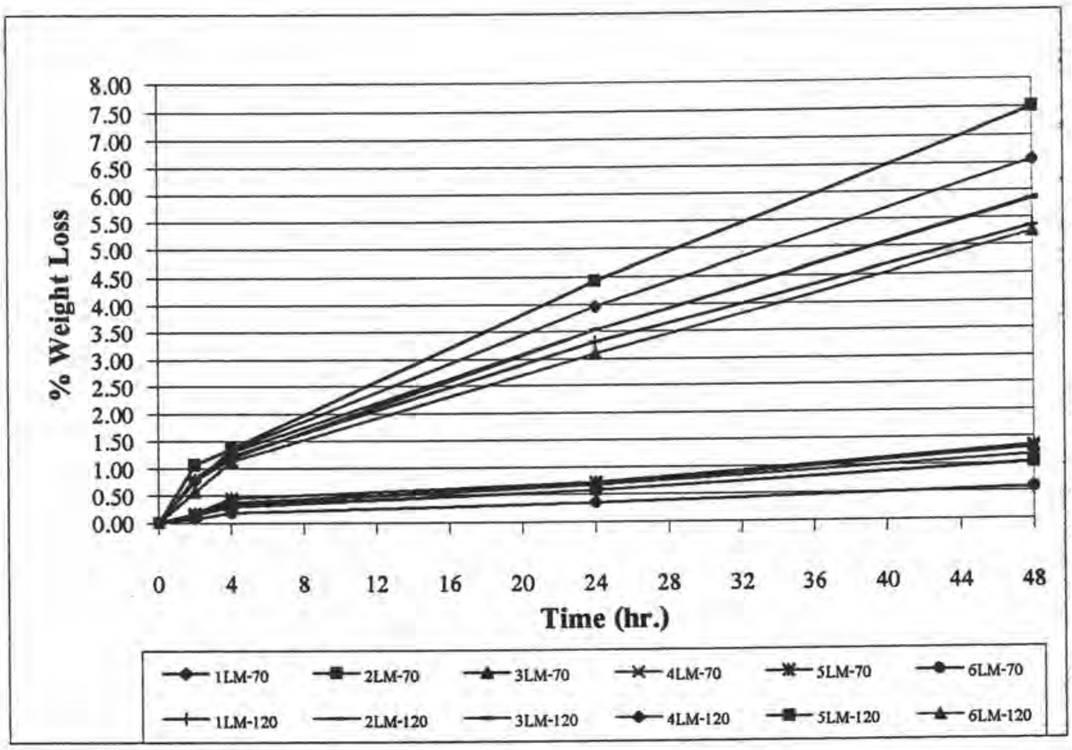

Figure 4.10: Plot of percentages of weight loss of PVC compounds versus immersion times in low viscosity motor oil at 70°C and 120°C

From this experiment, it is clear that plasticizers migration is increased with increasing temperature, since the viscosity of oil medium is decreased so plasticizers can be migrated easily from PVC compounds into oil medium[9]. The loss of weight and shrinkage of the PVC specimens were observed at immersion time which is higher than 24 hours. This fact is indicated that the migration of plasticizers from PVC specimens is higher than the migration of oil into PVC. Hence the migration of plasticizers can be expressed in term of weight loss of PVC specimen. In addition, we can observe discoloration of PVC specimens after immersion at 48 hours, due to the degradation effect.

Six formulations of flexible PVC compound can be readily compared as followed:

1. Plasticizers migration is increased significantly when comparing oil ageing test at $70^{\circ}C$ to $120^{\circ}C$ (as shown in Figure 4.10).
2. Formulation 6 has less plasticizer migration than the other formulations. Comparing formulation with the same hardness (Formulation 2 to 5), Formulation 2 has less plasticizer migration (as shown in Figure 4.2 to 4.9).

Oil ageing test at $70^{\circ}C$ and $120^{\circ}C$ are also compared in other oils. The results of plasticizers migration are similarly, so they are not shown at here (see Appendix C).

4.4 Effect of Oil Ageing on hardness of PVC compounds

The efficiency of the plasticizers was studied by determining the hardness. The shore A Hardness of PVC specimens was measured in term of penetration distance after a 15 second delay by using ASTM D-2240 method, before and after oil ageing test at 70 °C and 120 °C for 4 and 48 hours. The results are shown in Table 3 and 4 (data of Table 1D to 12D in Appendix D) respectively.

Table 4.3: Average of hardness of PVC compounds before and after oil ageing test in various oils at 70°C for 4 and 48 hours

	LM				HM				LS				HS			
Formulation	0 hr.	4 hr.	0 hr.	48 hr.	0 hr.	4 hr.	0 hr.	48 hr.	0 hr.	4 hr.	0 hr.	48 hr.	0 hr.	4 hr.	0 hr.	48 hr.
1	80.5	81.7	80.7	83.8	80.6	81.5	81.1	84.6	80.5	81.6	80.5	83.4	80.4	81.0	80.4	83.5
2	80.8	81.6	80.2	84.5	81.3	82.1	81.4	85.6	81.3	81.7	81.3	84.3	81.5	81.6	81.5	84.5
3	80.9	81.8	81.2	84.8	81.3	82.0	81.3	85.0	80.8	82.6	81.6	83.1	81.5	81.7	81.3	83.7
4	80.6	81.7	80.6	84.9	80.8	82.0	81.1	84.0	80.5	81.6	80.6	83.3	80.4	81.5	80.6	83.2
5	80.6	81.9	80.9	84.3	80.7	81.9	80.7	84.0	80.3	81.4	80.7	83.5	80.5	81.4	80.6	83.4
6	91.1	91.9	91.3	95.6	90.6	92.0	91.0	94.5	90.2	92.4	89.8	94.4	89.9	93.6	90.2	94.4

Table 4.4: Average of hardness of PVC compounds before and after oil ageing test in various oils at 120°C for 4 hours

	LM		HM		LS		HS	
Formulation	0 hr.	4 hr.	0 hr.	4 hr.	0 hr.	4 hr.	0 hr.	4 hr.
1	80.6	85.4	80.4	86.5	80.3	85.9	80.4	86.6
2	80.4	86.8	80.4	86.6	80.4	86.5	80.5	86.9
3	80.5	86.5	80.4	85.9	80.4	86.6	80.5	86.3
4	80.5	86.4	80.5	85.2	80.5	86.6	80.5	87.2
5	80.4	86.4	80.4	85.7	80.4	86.6	80.2	86.3
6	90.6	95.5	90.4	95.5	90.6	96.4	90.5	97.2

It can be observed that PVC compound with 50 phr of DOP has hardness 80A, while PVC compound with 50 phr of chlorinated paraffin has hardness 90A.

To achieve hardness 80A, more 50 phr of chlorinated paraffin need be used. It can be concluded that DOP has higher plasticized efficiency to PVC compound than chlorinated paraffin.

From Table 4.3 and 4.4 as expected that all PVC compound formulations has higher hardness as increasing oil ageing temperature and time due to plasticizers migration. Degradation and shrinkage of PVC compound can be observed after oil ageing test at 120°C for 48 hours, which is seen from discoloration and distortion of PVC specimens. So the corrected hardness can not be measured (expected hardness is higher than 97A).

4.5 Determination of Compatibility of Plasticizers and PVC resins by Fusion Characteristic

The compatibility of a plasticizers and PVC resins is the result of the interaction between them. And it can be measured as fusion of PVC compound[7]. Each dry blend of six formulations as shown in Table 4.2 was added to the preheated Brabender Torque Rheometer at 140 °C.

When the plasticizers began to solvate the surface of PVC resin particles, the resistance to mixing increased rapidly. This can be observed as an increasing in torque. The peak is sharp and occurs approximately at the point where fusion is complete. Following the peak, the melt viscosity decreases with mixing temperature or time. So, fusion of PVC compound is depended on the thermal history, pressure and shear experienced by the polymer as it was processed. The typical torque-temperature curved obtained for the PVC and plasticizer blends are shown in Table 1E to 19E (see Appendix E). Figure 4.11 showed the plotted of torque and time of PVC compounds after fusion test.

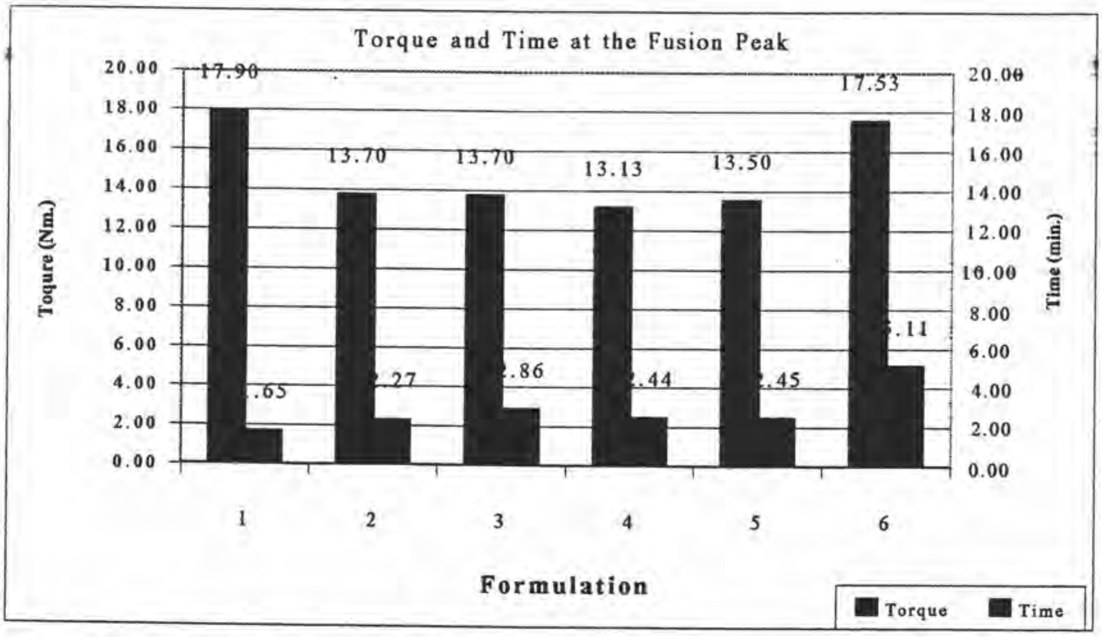

Figure 4.11: Plot of torque and time of six formulations of PVC compounds after fusion test

It can be observed that fusion time of Formulation 1 to 5 is shorter than Formulation 6 and torque of Formulation 2 to 5 is lower than Formulation 1 and 6 due to the compatibility of plasticizer and PVC resins[7].

From this result, Formulation 2 is melted completely in short time and low power requirement. Hence Formulation 2 has compromised processing condition between fusion time and torque, which has plasticizer blends between DOP and chlorinated paraffin at the ratio of 45:5 phr. It can be gave a high productivity.

4.6 Determination of Flammability Test of PVC compounds

Flammability property of flexible PVC compounds is measured in term of oxygen index according to ASTM D-2863. This method measured the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that would just support flaming combustion.

Figure 4.12 showed the plotted of oxygen index of six formulations of PVC compounds as shown in Table 4.2. Details are shown in Table 20E (see Appendix E).

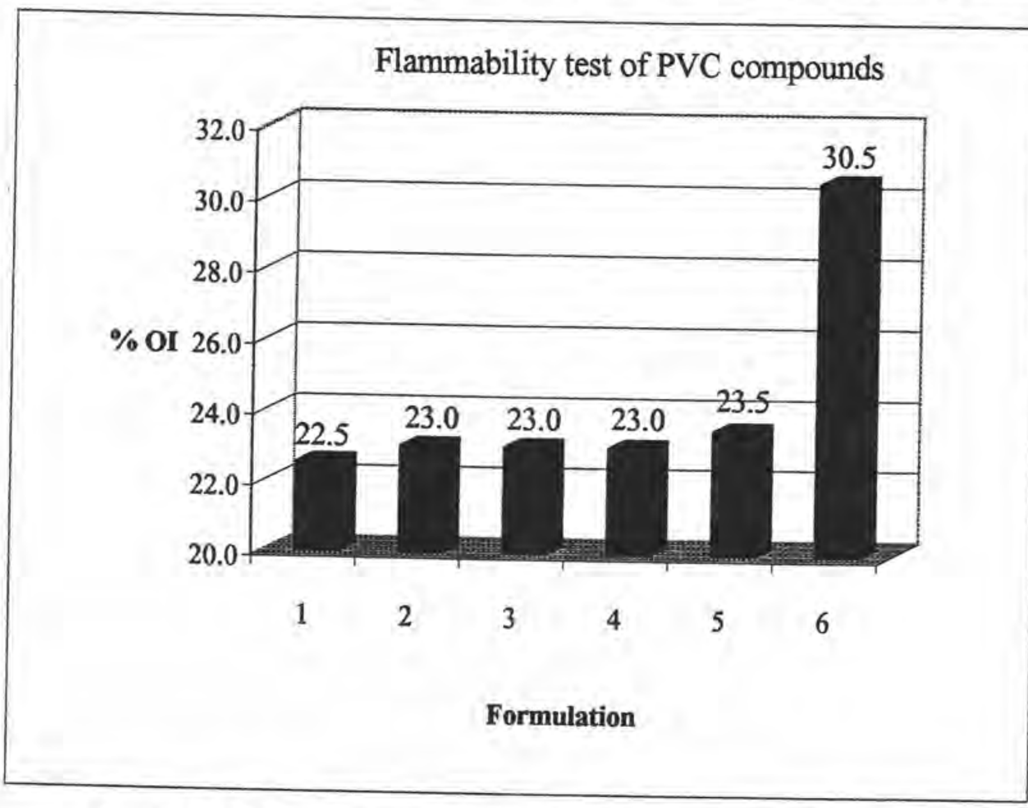

Figure 4.12: Plot of Oxygen index of six formulations of PVC compounds

Formulation 1, which has only DOP as plasticizer, has the lowest oxygen index as 22.5. While Formulation 6, which has only chlorinated paraffin as plasticizer, has the highest oxygen index as 30.5. Formulation 2 to 5, which are plasticizer blends, has same hardness 80A as Formulation 1, can little improve of oxygen index from 22.5 to 23.5.

This is one of the difficulties of using chlorinated paraffin, which has chlorine content to improve the flame retardant of flexible PVC compounds by maintaining the hardness. Because organic plasticizer like DOP, which give higher flexibility of PVC compound can minimize the flammability when using small portion of chlorinated paraffin.

4.7 Effect of Oil Ageing on Tensile Properties

Five dumbbell of six PVC compound formulations as shown in Table 4.2 are immersed in various oils: low and high viscosity motor oils and silicone oils at 70°C for 4 hours according to ASTM D-638.

After applied tensile force (stress) to PVC specimens, they are deformed or stretched in the direction of force. All tensile properties, i.e., tensile strength at break, modulus, tensile stress at one hundred percentages of elongation and elongation at break, are automatically calculated with computing software.

Figure 4.13 showed the percentages of retention of tensile strength of six PVC compound formulations after oil ageing test at 70°C for 4 hours. Details of tensile strength before and after oil ageing test are shown in Table 1F (see Appendix F).

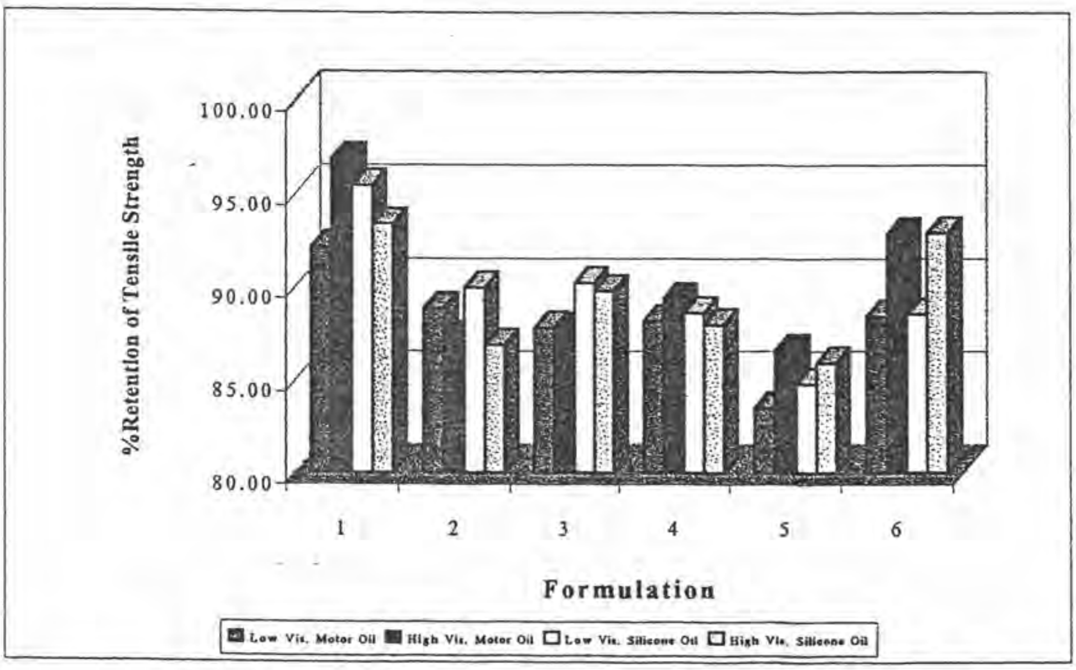

Figure 4.13: Plot of percentages of retention of tensile strength of six PVC compound formulations after oil ageing test

Figure 4.13 showed that Formulation 1, which has only 50 phr of DOP as plasticizer, exhibited the highest percentages of retention of tensile strength in various oils than the others. Comparing plasticizer blends in Formulation 2 to 5, it is found that Formulation 5, which has plasticizer blends between DOP and chlorinated paraffin at 35:20 phr, exhibited the lowest percentages of retention of tensile strength. While, Formulation 2 to 4 has almost the same percentages of retention tensile strength.

Figure 4.14 showed the percentages of retention of modulus of six PVC compound formulations after oil ageing test at 70°C for 4 hours. Details of modulus before and after oil ageing test are shown in Table 3F (see Appendix F).

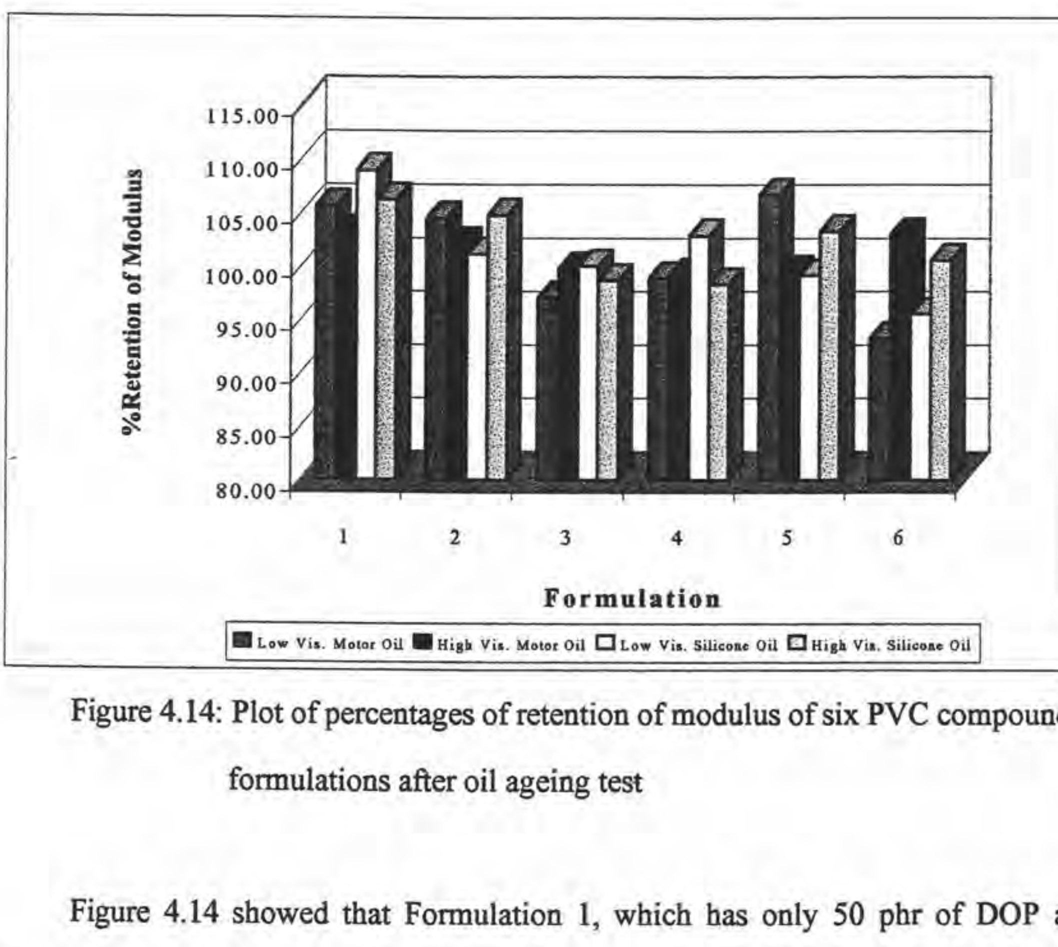

Figure 4.14: Plot of percentages of retention of modulus of six PVC compound formulations after oil ageing test

Figure 4.14 showed that Formulation 1, which has only 50 phr of DOP as plasticizer, exhibited the highest percentages of retention of modulus in various oils than the others. Comparing plasticizer blends in Formulation 2 to 5, it is found that Formulation 2, which has plasticizer blends between DOP and chlorinated paraffin at 45:5 phr, exhibited the highest percentages of retention of modulus than the rest.

Figure 4.15 showed the percentages of retention of elongation at break of six PVC compound formulations after oil ageing test at 70°C for 4 hours. Details of elongation at break before and after oil ageing test are shown in Table 5F (see Appendix F).

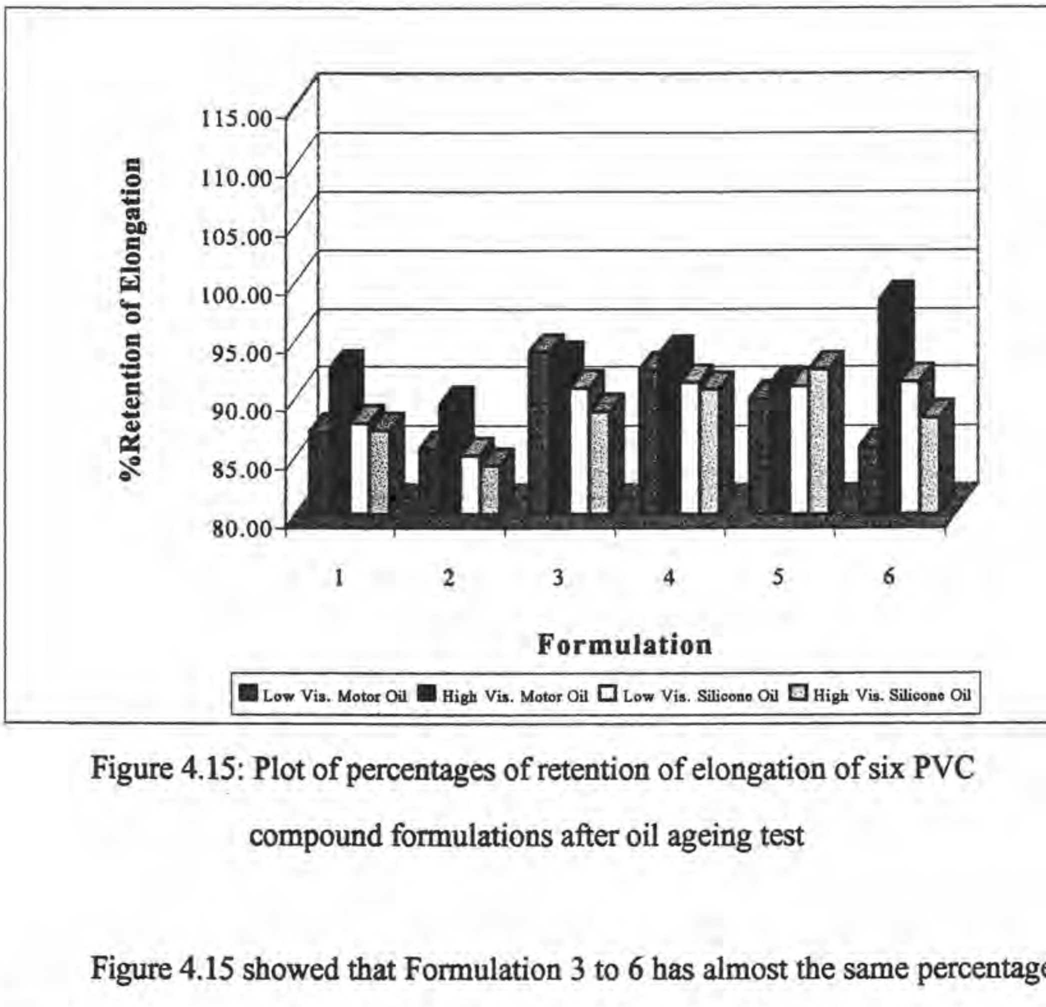

Figure 4.15: Plot of percentages of retention of elongation of six PVC compound formulations after oil ageing test

Figure 4.15 showed that Formulation 3 to 6 has almost the same percentages of retention of elongation at break and are higher than the others. Following by Formulation 6, 1 and 2 respectively.

Figure 4.16 showed the percentages of retention of tensile strength at one hundred percentages of elongation of six PVC compound formulations after oil ageing test at 70°C for 4 hours. Details of tensile strength at one hundred percentages of elongation before and after oil ageing test are shown in Table 7F (see Appendix F).

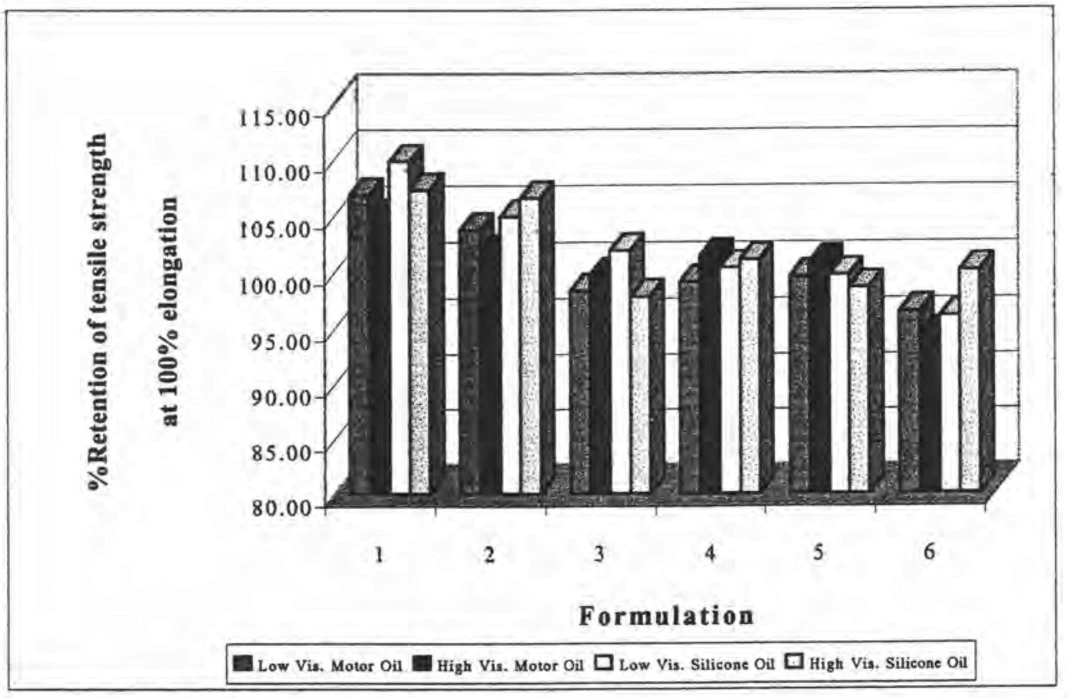

Figure 4.16: Plot of percentages of retention of tensile strength at one hundred percentages of elongation of six PVC compound formulations after oil ageing test

Figure 4.16 showed that Formulation 1, which has only 50 phr. of DOP as plasticizer, exhibited the highest percentages of retention of tensile strength at one hundred percentages of elongation in various oils than the others. Comparing plasticizer blends in Formulation 2 to 5, it is found that Formulation 2, which has plasticizer blends between DOP and chlorinated paraffin at 45:5 phr, exhibited higher percentages of retention of tensile strength at one hundred percentages of elongation.

The results of tensile properties are concluded as followed:

1) Formulation 1 has the highest percentages of retention of tensile strength at break than the others. Comparing plasticizer blends in Formulation 2 to 5, Formulation 2 has higher percentages of retention of tensile strength at break that the rest (as shown in Figure 4.13).

2) Formulation 1 has the highest percentages of retention of modulus than the others. Comparing plasticizer blends in Formulation 2 to 5, Formulation 2 has higher percentages of retention of modulus than the rest (as shown in Figure 4.14).
3) Formulation 1 has lower percentages of retention of elongation at break than Formulation 6. Comparing plasticizer blends in Formulation 2 to 5, Formulation 2 has the lowest percentages of retention of elongation at break than the others (as shown in Figure 4.15).
4) Formulation 1 has the highest percentages of retention of tensile strength at one hundred percentages of elongation than the others. Comparing plasticizer blends in Formulation 2 to 5, Formulation 2 has higher percentages of retention of tensile strength at one hundred percentages of elongation than the rest (as shown in Figure 4.16).

4.8 Effect of Oil Ageing on surface appearance of PVC compounds

Scanning electron microscope technique is used to observe the surface appearance of six PVC compound formulations as shown in Table 4.2. After they are immersion in various oils at 70°C for 4 hours, they are coated with conductive gold in an ionic splitter.

Figure 4.17 showed scanning electron micrograph of surface appearance of six PVC compound formulations after immersion in low viscosity motor oil. It is found that plasticizer migration form PVC compound to oil medium causes PVC specimens to have rough surface. As mentioned in section 4.4 (Effect of oil ageing on hardness of PVC compounds), plasticizers migration causes PVC specimens to have higher hardness and to be shrunken. These effects can be seen clearly in the other oils as shown in Figure 4.18 (high viscosity motor oil), Figure 4.19 (low viscosity silicone oil) and Figure 4.20 (high viscosity silicone oil).

Silicone oil is inert medium, which has a backbone of silicone and oxygen and also has symmetry molecule. It is found that plasticizer migration in low viscosity silicone oil is higher than in high viscosity one. This is due to the fact that plasticizers can migrate into low viscosity oil medium easier than high viscosity one.

In contrast it is found that plasticizers migration in high viscosity Motor oil is higher than low viscosity one. This can be explained from the molecular weight structure of motor oil is aromatic hydrocarbon, which is an active group. So, high viscosity motor oil, which has higher molecular weight than low viscosity one, has been effected on the migration of plasticizers more than the low viscosity one.

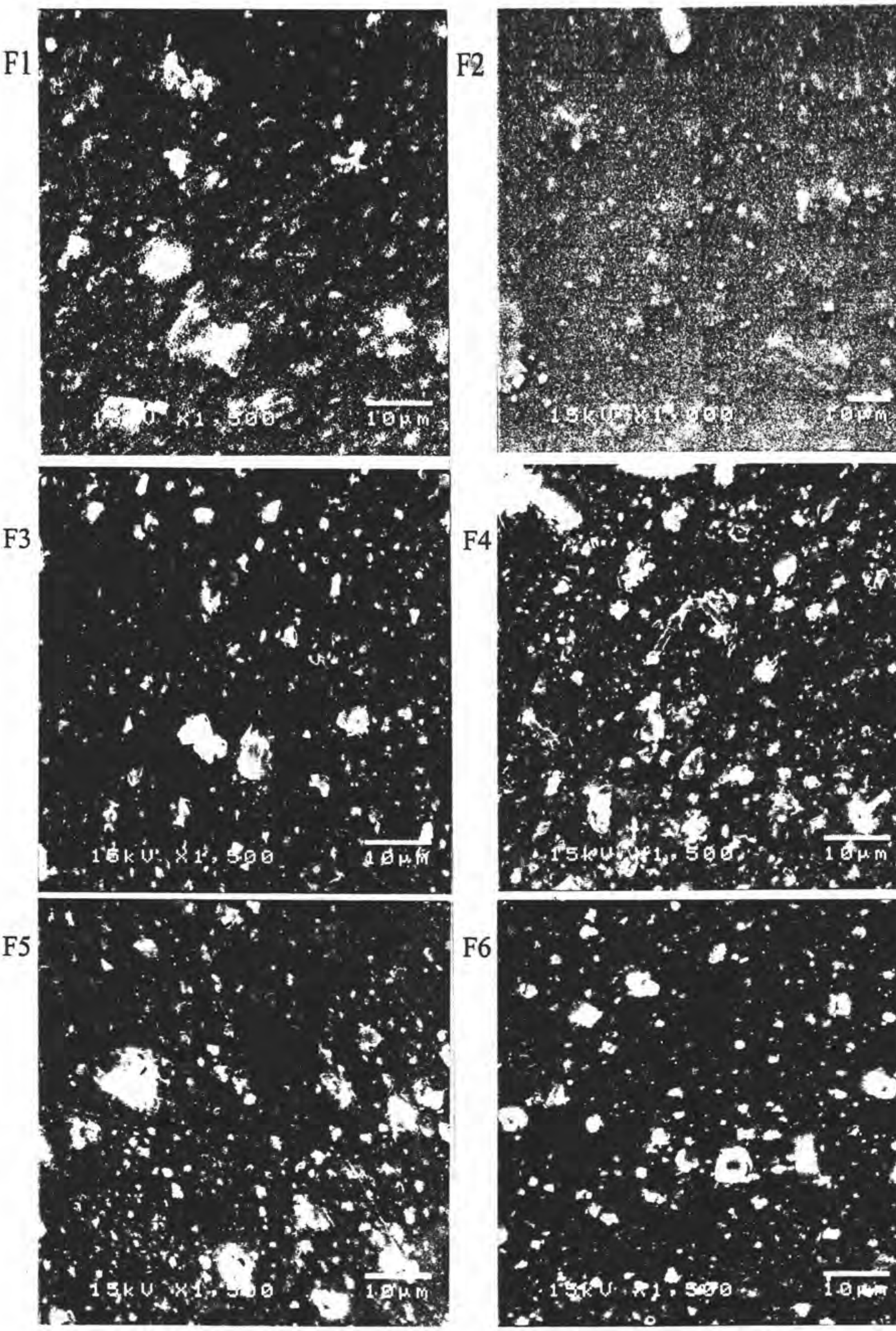

Figure 4.17: Scanning electron micrograph of surface appearance of six PVC compound formulations after immersion in low viscosity motor oil at 70°C for 4 hours. (F is Formulation)

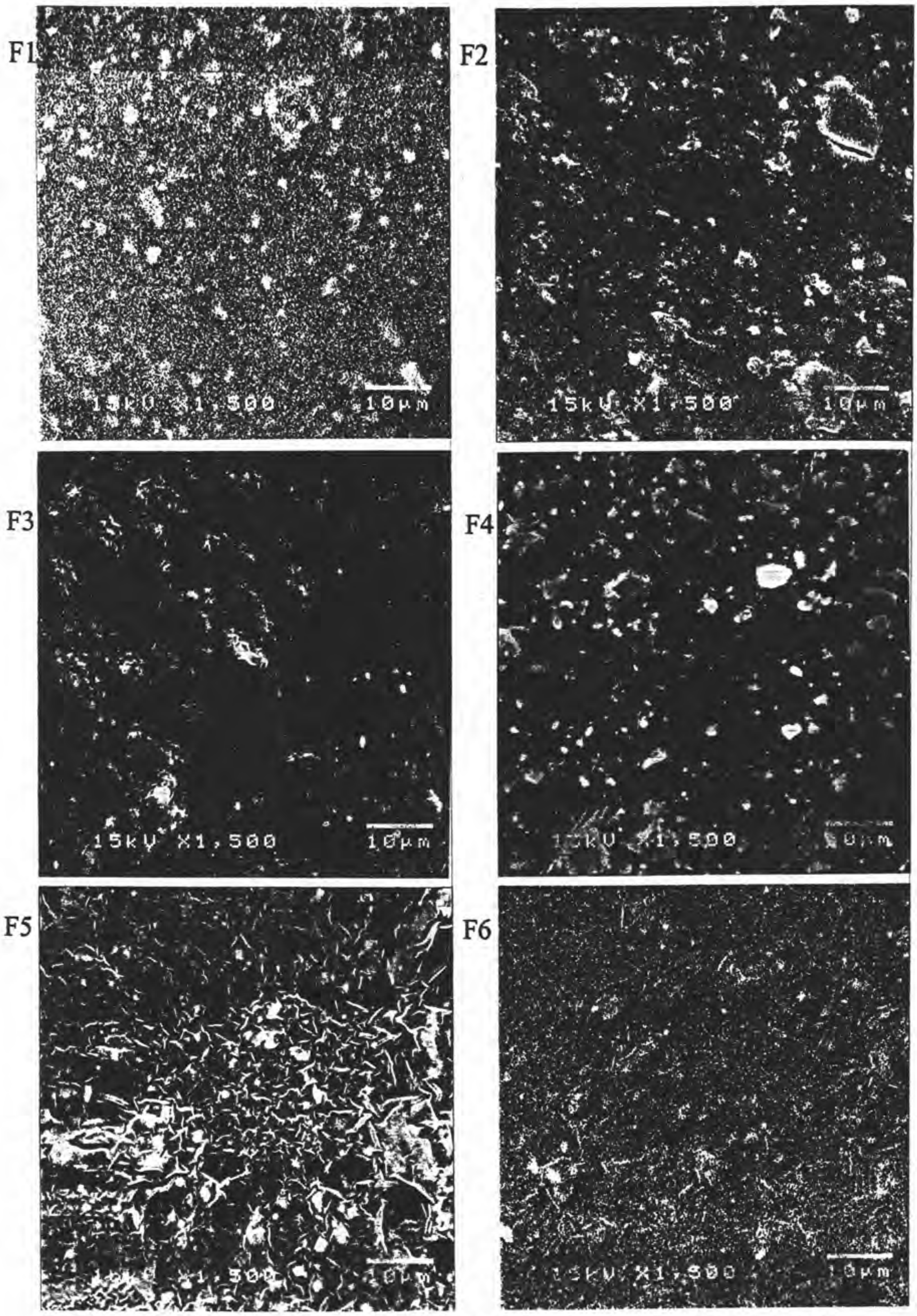

Figure 4.18: Scanning electron micrograph of surface appearance of six PVC compound formulations after immersion in high viscosity motor oil at 70°C for 4 hours.

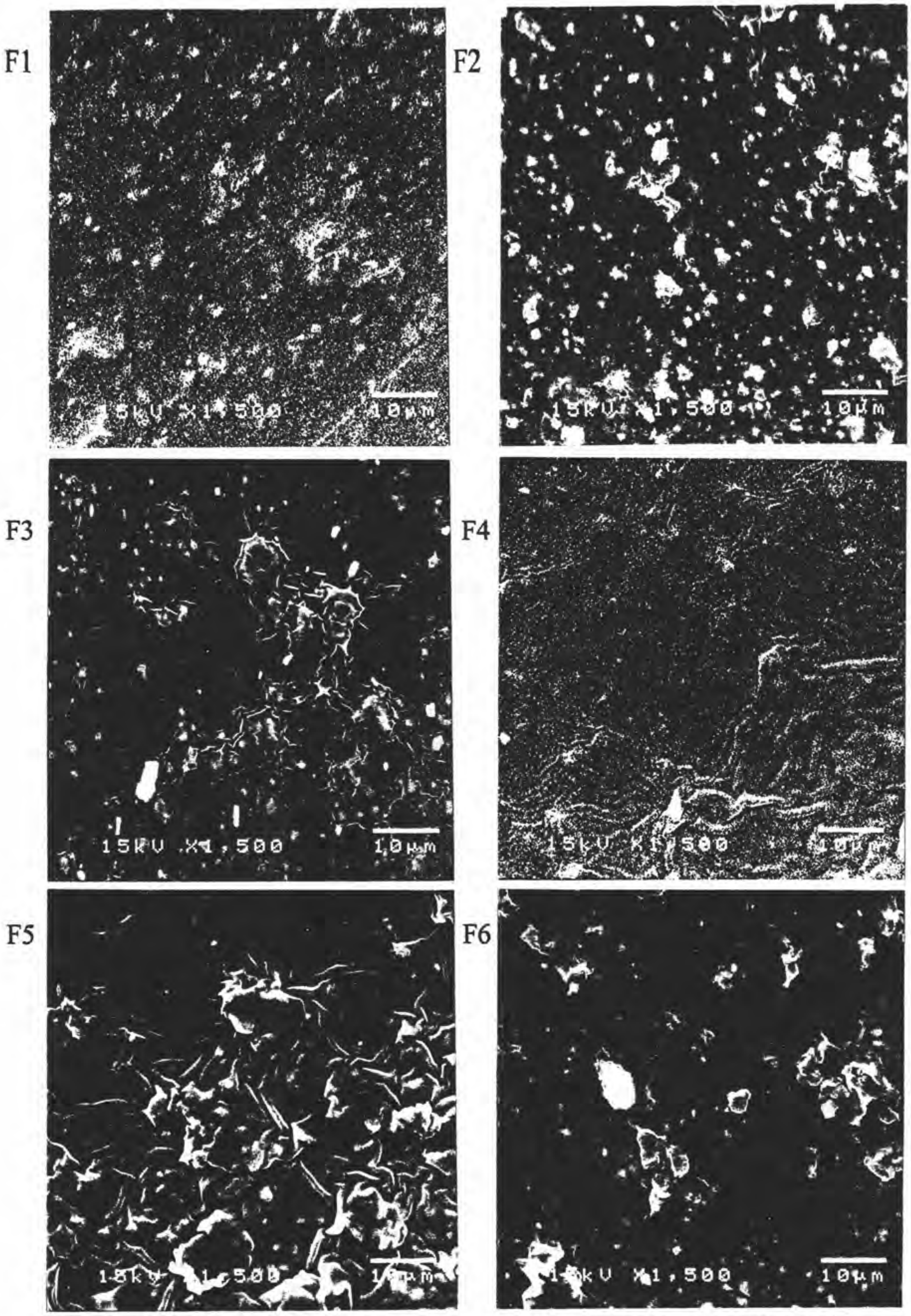

Figure 4.19: Scanning electron micrograph of surface appearance of six PVC compound formulations after immersion in low viscosity silicone oil at 70°C for 4 hours. (F is Formulation)

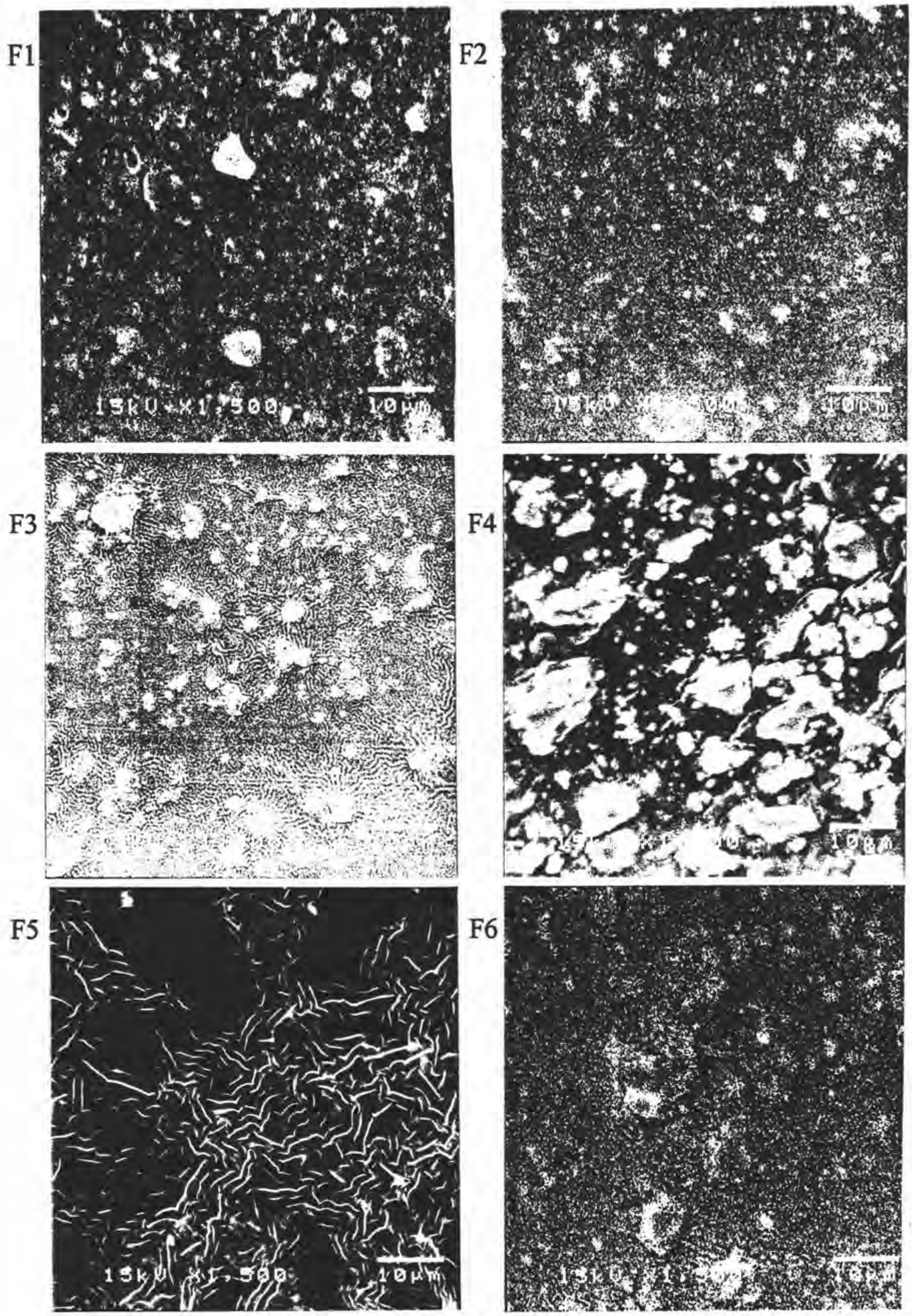

Figure 4.20: Scanning electron micrograph of surface appearance of six PVC compound formulations after immersion in high viscosity silicone oil at 70°C for 4 hours. (F is Formulation)