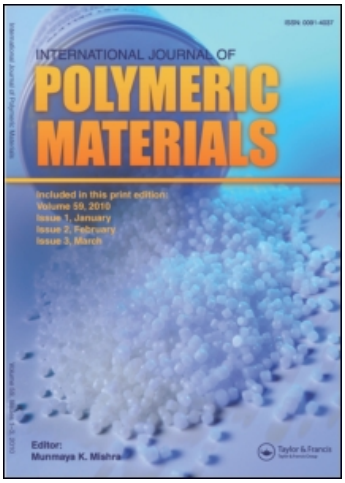


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# Plasticizer Extenders for Polyvinyl Chloride (PVC) Chlorinated Esters and Ether

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# Plasticizer Extenders for Polyvinyl Chloride (PVC) Chlorinated Esters and Ether†

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The preparation of chlorinated esters and an ether of a low cost indigenous raw material, 3-pentadecenyl phenol, is described. These chlorinated products have been further evaluated in PVC compounds as secondary plasticizers.

## INTRODUCTION

Chlorinated oil extracts, oil residues and fats[1] are considered as a most important group of plasticizer extenders, because of their low cost, low vapor pressure, flame resistance and excellent electrical properties. Due to the limited compatibility with vinyl resins, they are normally used in admixture with a primary plasticizer such as DOP. Apart from their important place in plastic industries, they are extensively used in cable, paint and metal lubricant industries.

Chlorinated products of phenol ethers[2] (Mollonc), hydrocarbons,[3] paraffins,[4] alkoxy benzenes,[5] biphenyls,[6] anthracene oil,[7] 3-pentadecenylphenyl acetate and 3-pentadecenylphenyl methyl ether,[8] mineral oil[9] etc. have been reported as plasticizer extenders

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for PVC. In recent years, Cereclors (chlorinated paraffins) are widely used as plasticizer extenders in PVC.

In the present study the following compounds have been synthesized and evaluated as plasticizer extenders in PVC.

(1) Chlorinated 3-pentadecenylphenyl stearate.
(2) Chlorinated 3-pentadecenylphenyl oleate.
(3) Chlorinated 3-pentadecenylphenyl linoleate.
(4) Chlorinated 3-pentadecenylphenyl phenyl ether.

## EXPERIMENTAL

### Preparation of esters and ether

The esters and ether were prepared from 3-pentadecenyl phenol as per the procedure described in our earlier communication.[10]



### General method for chlorination of esters and ether

Dry chlorine gas was passed through esters and ether at 0–5°C for a specified time (Table II). Then the product was diluted with a suitable volume of carbon tetrachloride and dry nitrogen gas was passed through it at room temperature (to drive off excess of chlorine gas). Finally the solvent was distilled off to get the residual chlorinated product. The chlorination of unsaturated esters was carried out without any difficulties because fully chlorine saturated esters were pourable liquids at 0–5°C. In the case of 3-pentadecenylphenyl phenyl ether the aromatic nuclei were not fully saturated with chlorine at the end of the chlorination as at this stage the compound was very viscous.

The chlorination of these products was also carried out in solvent medium such as carbon tetrachloride but showed no advantage over direct chlorination without solvent. The elemental analysis of the respective chlorinated products is given in Table II.

### Compounding and testing

The compounding recipe used in the evaluation program of the chlorinated esters and ether of 3-pentadecenyl phenol, as extenders, is given in Table I.

TABLE I
Compounding recipe

| No. | Ingredients | Parts |
|---|---|---|
| 1 | PVC resin[a] | 100 |
| 2 | Plasticizer DOP-extender (2/1) | variable |
| 3 | White lead paste | 8 |
| 4 | Calcium stearate | 1 |
| 5 | Stearic acid | 1 |

[a] A product of M/s. Sriram Vinyls, Kota, India having K value of 66.

Initially the extender was dissolved in a primary plasticizer (DOP) in the ratio of 1/2. Then the PVC resin was thoroughly mixed with plasticizer-extender mixture and other ingredients in a mixer.

The plasticizer-extender mixture was blended in the proportions of 40, 50, 60 and 70 parts with 100 parts of resin for evaluation. The compound was milled at 150°C for 6 minutes on a two roll mixing mill to give uniform sheet of thickness between 0.01 to 0.025 inch. The tensile strength, modulus, elongation and hardness were determined at room temperature according to ASTM designations D-412-68 and D-2240-68. The loss of plasticizer was determined according to ASTM designation D-1203 (61T) 1964. Volume resistivity was determined according to ASTM designation D-257-61 (1965).



## DISCUSSION

Aliphatic monoesters and diesters have limited compatability with polyvinyl chloride. Chemical groups that enhance the solvency for PVC, i.e. 'Plasticizer-polymer interaction', are generally believed to increase the compatability while groups that interfere with solvency reduce the compatibility. The presence of polar and polarizable groups such as aromatic, halide, oxirane and ester in the plasticizer enhance the solvency for PVC. In our previous communication[10] we have reported esters and ether of 3-pentadecenyl phenol as plasticizer extenders in PVC. In the present study it was decided to incorporate polar groups in the esters and ether of 3-pentadecenyl phenol by chlorination and evaluate them as plasticizer extenders in PVC.

TABLE II

Chlorinated esters and ether of 3-pentadecenyl phenol

| No. | Compound | Total period required for chlorination (hours) | Nature of the product | Analysis | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calculated | | | Found | | |
| | | | | C (%) | H (%) | Cl (%) | C (%) | H (%) | Cl (%) |
| I | Chlorinated 3-penta decenylphenyl stearate | 4 | Pale yellow viscous | 55.31 | 7.43 | 33.57 | 55.29 | 7.29 | 33.94 |
| II | Chlorinated 3-penta decenylphenyl oleate | 5 | Pale yellow viscous | 51.14 | 6.55 | 38.90 | 51.56 | 6.43 | 38.29 |
| III | Chlorinated 3-penta decenylphenyl linoleate | 8 | Pale yellow viscous | 47.55 | 5.89 | 43.29 | 47.49 | 5.76 | 43.06 |
| IV | Chlorinated 3-penta decenylphenyl phenyl ether | 9 | Pale yellow very viscous | — | — | — | 46.55 | 4.62 | 46.77 |

TABLE III

Physical properties of the PVC compounds A, B, C, D, E

| Physical properties | A | | B | | C | | D | | E | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] |
| 1. Hardness | 76 | 78 | 78 | 76 | 74 | 77 | 79 | 83 | 80 | 81 |
| 2. Tensile strength (MPa) | 16.41 | 18.27 | 17.03 | 18.68 | 17.86 | 19.37 | 21.18 | 22.20 | 17.51 | 18.55 |
| 3. 100% Modulus (MPa) | 12.68 | 14.48 | 13.03 | 15.03 | 13.51 | 15.51 | 16.75 | 18.00 | 13.24 | 15.72 |
| 4. Elongation % | 210 | 150 | 220 | 200 | 240 | 210 | 300 | 270 | 200 | 190 |
| 5. % loss in heating with carbon black at 70°C for 24 h | 1.225 | — | 1.272 | — | 1.760 | — | 1.015 | — | 1.446 | — |
| 6. % loss on aging in oven at 100°C for 24 h | 8.062 | — | 7.563 | — | 7.256 | — | 5.639 | — | 8.001 | — |
| 7. % loss in 1% Soap Solution at 25°C for 24 h | 0.1263 | — | 0.1247 | — | 0.1198 | — | 0.0988 | — | 0.1244 | — |
| 8. Volume resistance at 25°C (Ω cm) | $9.005 \times 10^{11}$ | — | $9.747 \times 10^{11}$ | — | $2.956 \times 10^{12}$ | — | $9.149 \times 10^{12}$ | — | $6.372 \times 10^{11}$ | — |

A = 40 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl stearate.
B = 40 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl oleate.
C = 40 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl linoleate.
D = 40 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl phenyl ether.
E = 40 parts of dioctyl phthalate.
[a] Before aging.
[b] After aging at 100°C for 24 h.

TABLE IV

Physical properties of the PVC compounds A–I, B–I, C–I, D–I, and E–I

| Physical properties | A–I | | B–I | | C–I | | D–I | | E–I | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] | (1)[a] | (2)[b] |
| 1. Hardness | 74 | 76 | 73 | 74 | 70 | 72 | 75 | 78 | 76 | 79 |
| 2. Tensile strength (MPa) | 15.79 | 16.89 | 16.13 | 17.65 | 16.96 | 18.27 | 19.51 | 20.41 | 16.96 | 17.51 |
| 3. 100% Modulus (MPa) | 12.34 | 13.72 | 11.93 | 14.13 | 12.89 | 14.96 | 16.00 | 17.51 | 12.62 | 14.48 |
| 4. Elongation % | 230 | 210 | 250 | 230 | 260 | 240 | 350 | 290 | 260 | 230 |
| 5. % loss in heating with carbon black at 70°C for 24 h | 1.687 | — | 1.773 | — | 1.663 | — | 1.285 | — | 1.877 | — |
| 6. % loss on aging in oven at 100°C for 24 h | 9.222 | — | 8.459 | — | 7.645 | — | 6.599 | — | 10.660 | — |
| 7. % loss in 1% Soap Solution at 25°C for 24 h | 0.1700 | — | 0.1699 | — | 0.1566 | — | 0.1272 | — | 0.2101 | — |
| 8. Volume resistance at 25°C (Ω cm) | $5.495 \times 10^{11}$ | — | $1.122 \times 10^{11}$ | — | $1.140 \times 10^{12}$ | — | $8.308 \times 10^{12}$ | — | $4.800 \times 10^{11}$ | — |

A–I = 50 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl stearate.
B–I = 50 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl oleate.
C–I = 50 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl linoleate.
D–I = 50 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl phenyl ether.
E–I = 50 parts of dioctyl phthalate.
[a] Before aging.
[b] After aging at 100°C for 24 h.

TABLE V

Physical properties of the PVC compounds A–II, B–II, C–II, D–II and E–II

| Physical properties | A–II (1)[a] | A–II (2)[b] | B–II (1)[a] | B–II (2)[b] | C–II (1)[a] | C–II (2)[b] | D–II (1)[a] | D–II (2)[b] | E–II (1)[a] | E–II (2)[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Hardness | 69 | 70 | 70 | 72 | 68 | 70 | 68 | 71 | 65 | 68 |
| 2. Tensile strength (MPa) | 14.34 | 15.24 | 14.48 | 15.79 | 15.51 | 16.89 | 19.17 | 20.13 | 14.13 | 16.34 |
| 3. 100% Modulus (MPa) | 11.10 | 12.00 | 11.03 | 12.13 | 12.13 | 13.10 | 15.79 | 16.82 | 10.13 | 11.24 |
| 4. Elongation % | 260 | 230 | 260 | 250 | 280 | 250 | 380 | 310 | 270 | 240 |
| 5. % loss in heating with carbon black at 70°C for 24 h | 2.096 | — | 1.946 | — | 1.742 | — | 1.332 | — | 2.178 | — |
| 6. % loss on aging in oven at 100°C for 24 h | 11.286 | — | 10.480 | — | 8.600 | — | 7.287 | — | 11.700 | — |
| 7. % loss in 1% Soap Solution at 25°C for 24 h | 0.2093 | — | 0.1964 | — | 0.1956 | — | 0.1375 | — | 0.2737 | — |
| 8. Volume resistance at 25°C (Ω cm) | $3.677 \times 10^{11}$ | — | $5.160 \times 10^{11}$ | — | $1.058 \times 10^{12}$ | — | $6.966 \times 10^{12}$ | — | $3.800 \times 10^{11}$ | — |

A–II = 60 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl stearate.
B–II = 60 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl oleate.
C–II = 60 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl linoleate.
D–II = 60 parts of mixture of DOP: Chlorinated 3-pentadecenylphenyl phenyl ether.
E–II = 60 parts of dioctyl phthalate.
[a] Before aging.
[b] After aging at 100°C for 24 h.

TABLE VI

Physical properties of the PVC compounds A–III, B–III, C–III, D–III and E–III

| Physical properties | A–III (1)[a] | A–III (2)[b] | B–III (1)[a] | B–III (2)[b] | C–III (1)[a] | C–III (2)[b] | D–III (1)[a] | D–III (2)[b] | E–III (1)[a] | E–III (2)[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Hardness | 68 | 68 | 66 | 69 | 62 | 65 | 65 | 69 | 61 | 63 |
| 2. Tensile strength (MPa) | 13.37 | 14.52 | 13.65 | 14.96 | 14.82 | 16.13 | 18.34 | 19.65 | 12.06 | 14.82 |
| 3. 100% Modulus (MPa) | 9.93 | 11.24 | 9.65 | 11.03 | 10.20 | 12.20 | 14.48 | 15.72 | 8.00 | 9.93 |
| 4. Elongation % | 300 | 270 | 320 | 300 | 360 | 310 | 420 | 340 | 300 | 270 |
| 5. % loss in heating with carbon black at 70°C for 24 h | 2.450 | — | 2.241 | — | 2.092 | — | 1.722 | — | 2.480 | — |
| 6. % loss on aging in oven at 100°C for 24 h | 12.040 | — | 11.763 | — | 10.053 | — | 8.034 | — | 11.540 | — |
| 7. % loss in 1% soap solution at 25°C for 24 h | 0.2732 | — | 0.2226 | — | 0.2003 | — | 0.1500 | — | 0.3021 | — |
| 8. Volume resistance at 25°C (Ω cm) | $2.580 \times 10^{11}$ | — | $2.967 \times 10^{11}$ | — | $9.891 \times 10^{11}$ | — | $4.238 \times 10^{12}$ | — | $2.583 \times 10^{11}$ | — |

A–III = 70 parts of mixture of DOP: chlorinated 3-pentadecenylphenyl stearate.
B–III = 70 parts of mixture of DOP: chlorinated 3-pentadecenylphenyl oleate.
C–III = 70 parts of mixture of DOP: chlorinated 3-pentadecenylphenyl linoleate.
D–III = 70 parts of mixture of DOP: chlorinated 3-pentadecenylphenyl phenyl ether.
E–III = 70 parts of dioctyl phthalate.
[a] Before aging
[b] After aging at 100°C for 24 h.

TABLE VII

Percentage retention of the physical properties after aging of the PVC compounds at 100°C for 24 h

| Compound No. | Hardness | Tensile strength | 100% Modulus | Elongation |
|---|---|---|---|---|
| A | 102 | 111 | 114 | 71 |
| B | 102 | 109 | 115 | 90 |
| C | 104 | 108 | 114 | 87 |
| D | 105 | 105 | 107 | 90 |
| E | 101 | 105 | 118 | 95 |
| A–I | 102 | 107 | 110 | 91 |
| B–I | 101 | 109 | 118 | 92 |
| C–I | 102 | 107 | 113 | 92 |
| D–I | 104 | 104 | 109 | 82 |
| E–I | 104 | 103 | 114 | 86 |
| A–II | 101 | 106 | 103 | 88 |
| B–II | 102 | 109 | 110 | 96 |
| C–II | 102 | 108 | 108 | 89 |
| D–II | 104 | 105 | 106 | 81 |
| E–II | 104 | 115 | 110 | 88 |
| A–III | 104 | 109 | 113 | 90 |
| B–III | 104 | 109 | 114 | 93 |
| C–III | 104 | 108 | 119 | 88 |
| D–III | 106 | 107 | 108 | 80 |
| E–III | 103 | 122 | 124 | 90 |



The chlorinated esters and ether are pale yellow liquids of medium to high viscosity and have 33 to 46% chlorine content. When compounded with PVC for use as primary plasticizer, they were found to be less compatible than DOP. Therefore they were evaluated as secondary plasticizers in PVC.

The results in Tables III to VI indicate that all the chlorinated products of 3-pentadecenyl phenol in combination with DOP (primary plasticizer) in the proportion of 1/2 show higher permanence than the PVC compounds where DOP alone is the plasticizer. This may be attributed to the polar nature of the compounds which possibly enhance their ability to tie up polar sites on the polymer chain. The higher strength and volume resistivity of the PVC compounds wherein chlorinated 3-pentadecenylphenyl phenyl ether has been used as secondary plasticizer may be due to its more polar nature (chlorine content 46%).

It would be seen from Table VII that the percentage retention of

the physical properties after aging of the PVC compounds (A to D), (A-I to D-I), (A-II to D-II), (A-III to D-III) wherein chlorinated esters and ether of 3-pentadecenyl phenol have been used are in good comparison with the PVC compounds (E, E-I, E-II, E-III) where DOP has been used as the only plasticizer.

## CONCLUSION

The level of plasticizer required to produce a given hardness, flexibility or modulus is often used as a measure of efficiency. Thus the efficiency of the chlorinated products of 3-pentadecenyl phenol as plasticizer extender can be indicated as chlorinated 3-pentadecenyl phenyl oleate > chlorinated 3-pentadecenylphenyl stearate > chlorinated 3-pentadecenylphenyl linoleate > chlorinated 3-pentadecenylphenyl phenyl ether.



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