712

Studies on epoxidised rubber seed oil as secondary plasticiser/stabiliser for polyvinyl chloride

R. Joseph[1], K. N. Madhusoodhanan[1], R. Alex[1], S. Varghese[1], K. E. George[2] and B. Kuriakose*[1]

Rubber seed oil (RSO) and epoxidised rubber seed oil (ERSO) were used as secondary plasticiser cum heat stabiliser in polyvinyl chloride (PVC). High temperature mixing studies, dynamic mechanical analysis, hot air aging tests and colour stability tests indicated that ERSO could be used as a less volatile secondary plasticiser and heat stabiliser for PVC in combination with dioctyl phthalate (DOP). The tensile properties of the compound containing 50 : 10 DOP/ERSO were found to be comparable to that containing 60 parts of DOP per 100 parts PVC.

Keywords: Epoxidised rubber seed oil, Polyvinyl chloride, Plasticiser, Stabiliser

Introduction

Rubber tree (*Hevea brasiliensis*) is widely used as the source of natural rubber and its seed has been found to be rich in oil. Fresh seed contains about 65% kernel and 35% shell.[1] Though there is variation in oil content of the seed from different clones, the average oil yield is about 42% of the weight of the dried kernel. Composition and characteristics of rubber seed oil vary with planting location and clone.[2] Rubber seed oil (RSO) is a light yellow, semidrying oil. The oil contains about 18–22% saturated and 78–82% unsaturated higher fatty acids. The composition of fatty acids present in RSO is given in Table 1.

There are various industrial applications for RSO. The oil is used for the production of factice.[3] Vijayagopalan and Gopalakrishnan[4] had reported the epoxidation of RSO with hydrogen peroxide and acetic acid. Epoxidised rubber seed oil (ERSO) is used in the formulations for anticorrosive coatings and adhesives.[5] RSO is also suitable for production of low quality soap.[6] Properties of rubber seed oil resemble those of linseed oil. It was therefore conceived as having strong potential for replacing linseed oil, partially in alkyd production.[7] Aigbodin *et al.*[8] have reported the use of RSO and ERSO in natural rubber compounds for improving the processability characteristics and physicomechanical properties.

Plasticisers are organic substances added to polymers to improve their flexibility and processability.[9] Plasticiser increases the softness, elongation and low temperature flexibility and decreases the concentration of intermolecular forces and the glass transition temperature T_g of polymers. They are classified into primary, secondary and extenders.[10] Esters, phosphates and epoxides are the most suitable plasticisers for PVC. Since PVC is polar in nature, mostly ester type plasticisers such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) are used for its compounds. Epoxidised vegetable oil is used both as a plasticiser and acid scavenger in PVC compounds to improve the resistance to thermal aging.

PVC is not thermally stable and beyond 100°C it degrades with the evolution of hydrochloric acid.[11] This process is further extended by the formation of conjugated and easily oxidisable double bonds along the chain which will result in the discolouration of the polymer.[12] The reactions involved are shown in Fig. 1.

Epoxidised soya bean oil, epoxidised oleic acid ester and other chemically modified vegetable oils are extensively used as stabilisers to improve the high temperature heat stability of PVC compounds.[13] Use of RSO, ERSO and its lead and barium salts as heat stabilisers for PVC has been reported by Okieimen and Ebhoaye.[14–16] In their trials, PVC was mixed with RSO, ERSO and its lead and barium salts and the compound heated in a nitrogen atmosphere. The polymer got degraded and the HCl evolved was absorbed in standard sodium hydroxide solution. The residual concentration of sodium hydroxide was then determined by titration with standard hydrochloric acid. Epoxides can be used as HCl scavengers and the reaction is expected to proceed by the neutralisation of HCl by epoxides.

This paper reports the results of a detailed study on the use of ERSO as a secondary plasticiser/stabiliser for PVC.

Experimental

Materials used

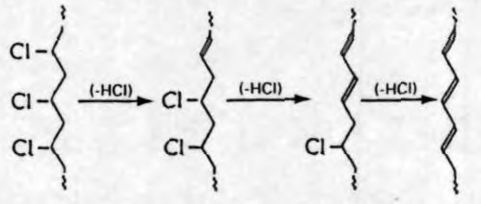
PVC resin (powder, emulsion grade, K value 65) used for the present study was supplied by Chemplast,

---

[1] Rubber Research Institute of India, Rubber Board P O, Kottayam 686 009, Kerala, India
[2] Cochin University of Science and Technology, Cochin 682 022, Kerala, India

*Corresponding author, email kuriakosebaby@hotmail.com

Published by Maney on behalf of the Institute
Received 19 November 2003; accepted 26 May 2004
DOI 10.1179/146580104225020974



1 **HCl evolution from PVC and formation of conjugated structure**

Chennai, India. Two types of PVC were used, 103 EP Grade and 103 EPM 7 Grade. Rubber seed oil was obtained from Virudhunagar. The quality parameters of rubber seed oil used for the present study are given in Table 2. ERSO of 5·0% epoxy content was prepared from RSO using hydrogen peroxide and formic acid as epoxidising agents at a temperature of 58–60°C.[8] Epoxidation level was determined by the acidimetric method.[17] All other chemicals used in the study were of commercial grade. Formulations of the compounds prepared are given in Table 3. RSO, ERSO and DOP were used as plasticisers in these compounds.

Preparation of compounds

The compounds for preparing test slabs were mixed in a 'Haake' Rheocord 90 for 6 min at 170°C and 60 rev min^{-1}. For assessing the effectiveness of ERSO and RSO as secondary plasticisers, formulations 1–5 given in Table 3 were used. Partial replacement of DOP with ERSO was attempted and standard graphs showing torque versus mixing time were plotted. The graphs obtained are shown in Figs. 2 and 3. For assessing the role of ERSO as a secondary plasticiser and stabiliser, mixes 6 to 9 were prepared (Table 3).

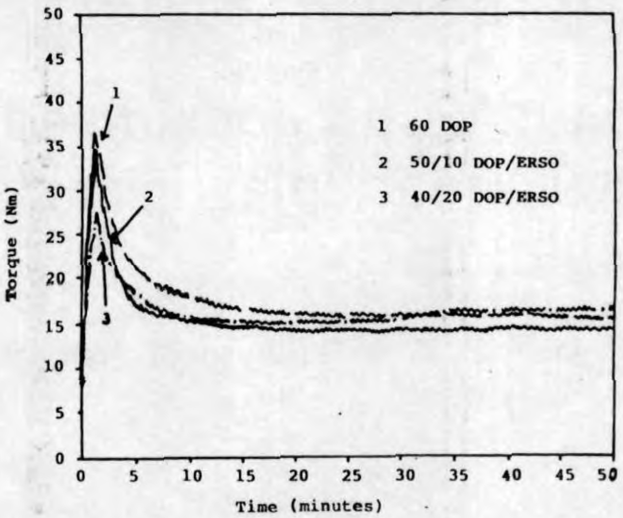
Table 1 Composition of fatty acids in rubber seed oil

Fatty acid	Content, %
Palmitic acid	10·8
Stearic acid	10·0
Oleic acid	23·5
Linoleic acid	38·5
Linolenic acid	16·2
Unidentified	1·0

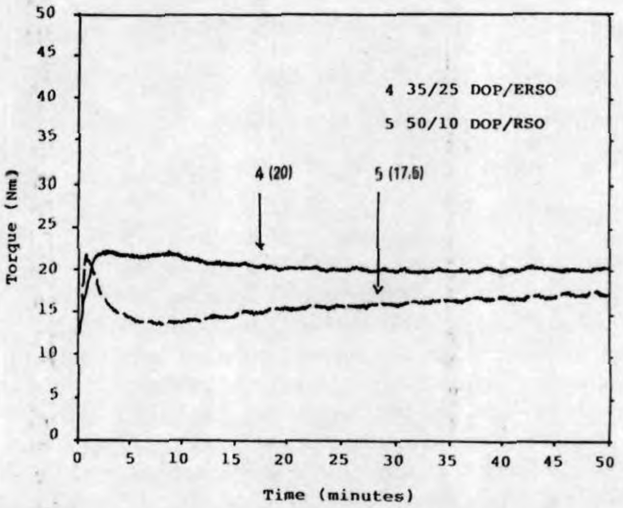
Table 2 Physical properties of rubber seed oil used

Parameter	Value
Acid value	36
Saponification value	191
Iodine value	132
Hydroxyl value	31
Unsaponifiables, %	0·80
Refractive index	1·47
Specific gravity (30°C)	0·92
Titre, °C	28

Titre is the solidifying temperature of the mixed fatty acids obtained from fat/oil.



2 **Mixing torque versus time plots for compounds 1–3**

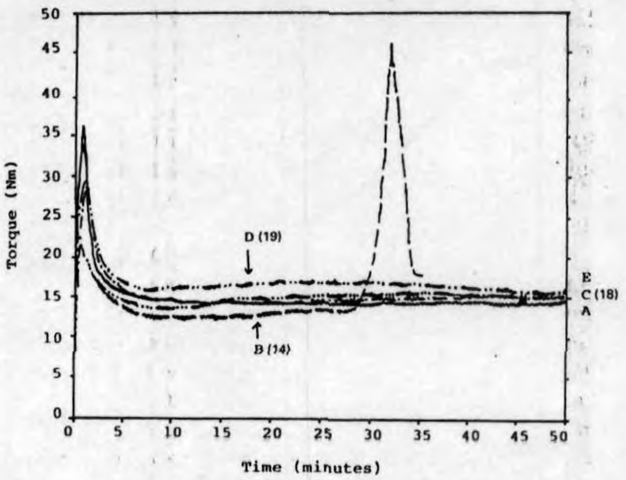


3 **Mixing torque versus time plots for compounds 4 and 5; figure given in brackets is stabilisation torque**

George *et al.*[18] had developed a stabiliser system for PVC containing a magnesium oxide/zinc oxide combination. In the study reported here, zinc oxide, magnesium oxide and stearic acid were partially replaced by ERSO, because ERSO could act as a secondary plasticiser/stabiliser (HCl scavenger). A control was prepared using tribasic lead sulphate (TBLS)/calcium stearate system. Formulations used are given in Table 4.

Table 3 Formulations for compounding

Ingredients	1	2	3	4	5	6	7	8	9	10
Polyvinyl chloride (103 EPM 7 grade)	100	100	100	100	100	100	100	100	100	100
Tribasic lead sulphate	3	3	3	3	3	2	2	–	–	–
Calcium stearate	1	1	1	1	1	1	1	1	1	1
Dioctyl phthalate	60	50	40	35	50	50	40	50	40	60
ERSO	–	10	20	25	–	10	20	10	20	–
RSO	–	–	–	–	10	–	–	–	–	–



4 **Mixing torque versus time plots for compounds A–E; figure given in brackets is degradation torque**

In this experiment, 103 EP grade PVC was used. The standard graphs showing torque versus mixing time (up to 50 min) were drawn (Fig. 4). The stabilising torque and degradation time were noted wherever applicable and are given in Table 5.

The samples used for preparing compounds for dynamic mechanical analysis are 1 to 3 and A to E.

Physical properties and aging resistance

Using the PVC compounds prepared in the 'Haake' Rheocord 90, test slabs were moulded at 170°C for 3 min in an electrically heated hydraulic press. Dumb-bell shaped testpieces were punched out from the sheets and tested for tensile properties, as per ASTM D 638-1999 using a 'Zwick' 1474 model Universal Testing Machine. Ageing resistance of the samples was determined by testing the tensile properties of the sample before and after aging at 100°C for 48 h. Results are given in Table 6.

The dynamic-mechanical thermal analyser (DMTA) spectra were recorded on rectangular specimens (length × width × thickness=$6\times1\times0\cdot25$ cm^3) in tensile mode at a frequency of 10 Hz using a Eplexor 150N device (Gabo Qualimeter, Testanlagen GmbH, Germany). DMTA spectra, namely storage and loss moduli and mechanical loss factor (tan δ) were recorded in the temperature range from −100 to 100°C at a heating rate of 2 K min^{-1}.

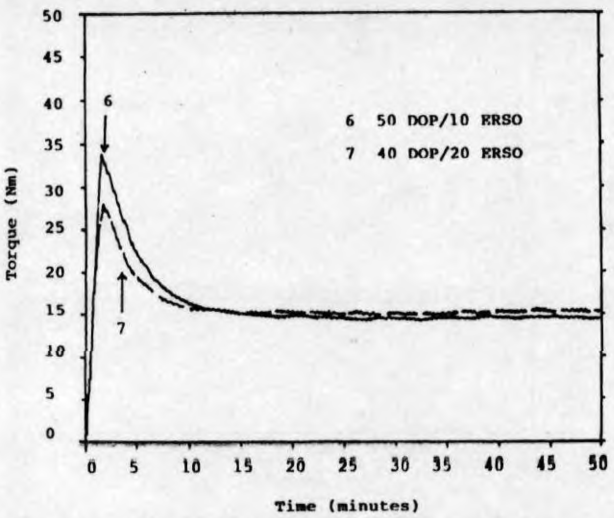
Heat stability

Dynamic heat stability

For testing dynamic heat stability of the compound, Rheocord traces were drawn using compounds prepared as per the formulations 6 and 7 (Table 3) which contained 1 part TBLS less than the control. There was no change in the stabilised torque for 50 min (Fig. 5). So compounds 8 and 9, which did not contain any TBLS were prepared and graphs showing torque

Table 4 Formulations (Series II)

Ingredients	A	B	C	D	E
Poly vinyl chloride (103 EP grade)	100	100	100	100	100
Tribasic lead sulphate	3	–	–	–	–
Calcium stearate	1	–	–	–	–
Magnesium oxide	–	4	4	2	2
Zinc oxide	–	4	4	4	2
Stearic acid	–	2	2	1	1
Dioctyl phthalate	60	60	50	50	40
ERSO	–	–	10	10	20



5 **Mixing torque versus time plots for compounds 6 and 7**

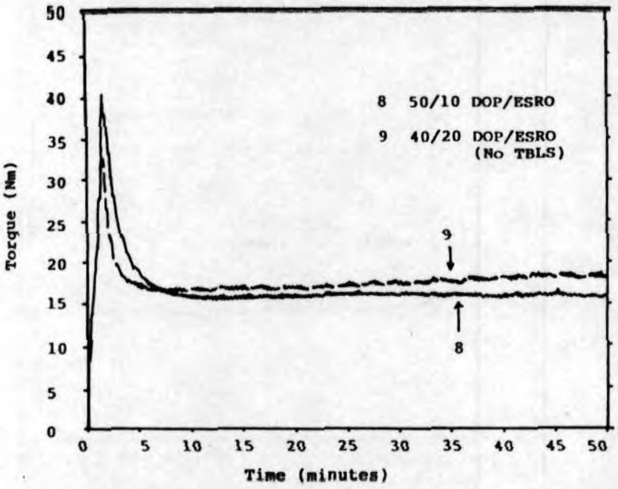
Table 5 Mixing characteristics of compounds

Compound number	Stabilising torque, N m	Degradation time, min
1	14	>50
2	15	>50
3	16	>50
4	17·5	>50
5	20	>50
6	14	>50
7	15	>50
8	15·5	>50
9	17·5	>50
A	18	>50
B	14	35
C	18	>50
D	19	>50
E	18	>50

Table 6 Tensile properties of compounds

Compound number		Tensile strength, MPa	Elongation at break, %	Modulus 100%, MPa	Modulus 200%, MPa
1	Ba	18·1	343	8·6	12·5
	Aa	19·6	385	7·6	12·1
2	Ba	19·6	322	10·1	14·3
	Aa	20·5	356	9·1	14·0
3	Ba	19·0	295	11·0	15·1
	Aa	20·4	317	11·1	15·8
A	Ba	15·8	244	8·4	13·9
	Aa	15·9	250	7·9	13·6
B	Ba	15·8	258	8·1	13·1
	Aa	15·4	264	7·5	12·5
C	Ba	15·6	252	8·8	13·5
	Aa	15·6	232	9·3	14·6
D	Ba	16·8	251	9·1	14·2
	Aa	16·9	238	9·3	14·4
E	Ba	15·6	261	9·6	13·7
	Aa	15·7	236	11·0	15·3

Aa, after aging; Ba, before aging.



6 Mixing torque versus time plots for compounds 8 and 9

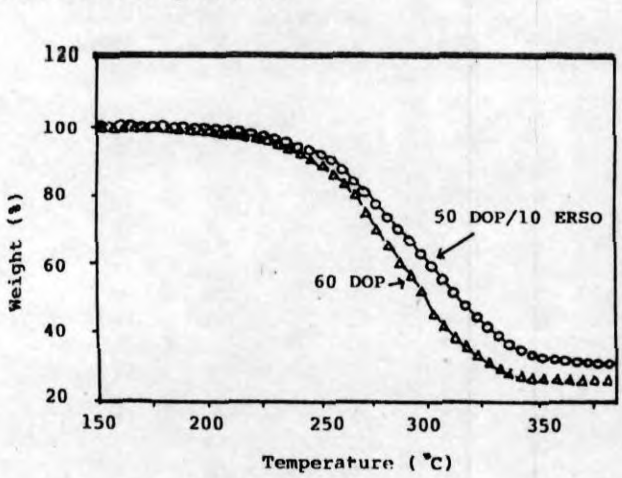
versus mixing time were drawn using 'Haake' Rheochord 90. In this case also, there was no change in stabilised torque for 50 min (Fig. 6).

Static heat stability

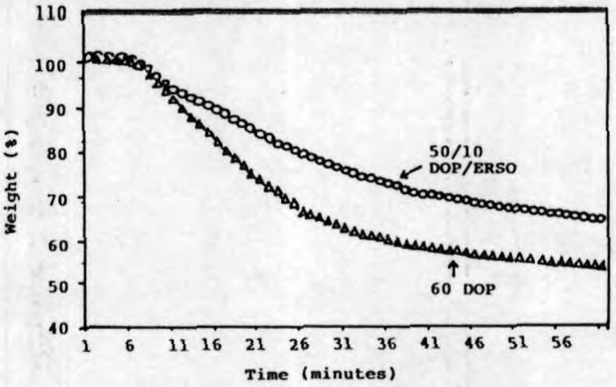
Volatilisation loss of the plasticiser was determined using a thermogravimetric analyzer (TGA). Thermograms were taken using 'Shimadzu' Model TGA-50 for compounds 1 and 2 and these are shown in Fig. 7 (samples change from light yellow to dark orange). Samples were heated at 250°C for 1 h and the isotherm plot is given in Fig. 8.

Colour test

For the colour test, samples were prepared from compounds 8 and A to E. Another compound, containing 60 parts of DOP and 1 part calcium stearate (without TBLS) was also prepared (compound 10) to compare with compound 8. During mixing in a 'Haake' Rheocord 90 at 170°C and 60 rev min^{-1}, samples were drawn at definite intervals, passed through a two-roll mill and moulded to the same thickness at 170°C. Optical photographs of the samples were taken and these are shown in Figs. 9 and 10. As there was a light yellow colour for ERSO, the original colour of samples 8, C, D and E was not pure white.



7 Mass retained versus temperature plots for compounds 1 and 2



8 Mass retained versus time plots for compounds 1 and 2 at 250°C

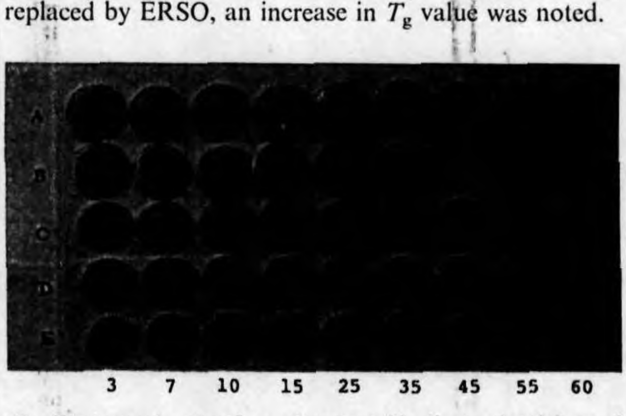
9 Photograph showing change with time of mixing of compounds 8 and 10

Results and discussion

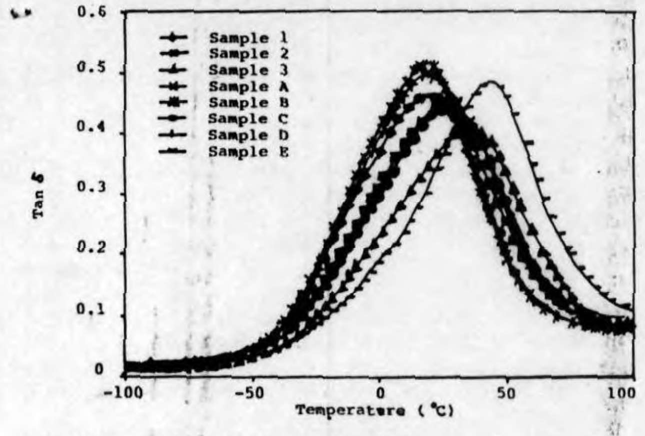
Effect of ERSO as secondary plasticiser

Mixing torque versus time plots given in Fig. 2 show that compounds 1, 2 and 3 have similar mixing behaviour and the stabilised torque values of compounds in which a part of DOP has been replaced by ERSO are only marginally higher than that containing DOP alone.

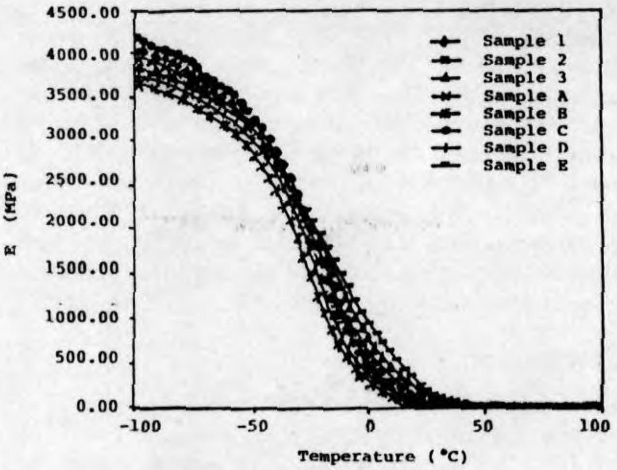
Compounds 4 and 5, which contained 25 parts ERSO and 10 parts RSO, respectively, had higher stabilising torque (Fig. 3) and they showed exudation of the plasticisers. Beyond 20 parts ERSO, the increase in torque seems to be greater, indicating 10 parts ERSO as the safe limit for replacing DOP. Also, without epoxidation, RSO cannot function as a secondary plasticiser. Hence, these compounds were not evaluated further. Figure 11 shows tan δ versus temperature plots of samples 1 to 3 and A to E. Replacement of 10 parts of DOP with ERSO gave almost comparable T_g values with that of sample containing 60 DOP. But in the case of samples 3 and E in which 20 parts of DOP was replaced by ERSO, an increase in T_g value was noted.



10 Photograph showing change with time of mixing of compounds A–E



11 Plots of tan δ versus temperature



12 Plots of elastic modulus versus temperature

Figure 12 shows the elastic modulus versus temperature plots of samples. In this case, samples containing 50 : 10 DOP/ERSO also showed comparable storage modulus values (E') to those containing 60 parts DOP, whereas samples 3 and E had higher modulus values. These observations further confirmed that 10 parts ERSO is the safe limit for replacing DOP in PVC compounds. The tensile properties of compounds 1, 2 and 3 given in Table 6 indicate that compounds 2 and 3, which contained combinations of DOP and ERSO, had almost the same tensile strength and the value is higher than that for compound 1, which contained DOP alone. The elastic modulus showed a regular increase from compound 1 to 3. This coupled with lower elongation at break values of compounds 2 and 3 indicated that the addition of ERSO as secondary plasticiser could be done only at a lower level of 10 to 15 parts per 100 PVC. The tensile properties of the samples after aging at 100°C for 48 h showed no appreciable change from the original tensile strength or modulus values of the sample before aging. These results indicate that ERSO could be used as a secondary plasticiser for PVC at lower levels without any adverse effect on processing characteristics and degradation of the sample. Compounds 6 and 7 which contained a lower dosage of stabiliser TBLS and compounds 8 and 9 which contained no TBLS also showed mixing characteristics almost similar to that of compound 1 (Table 5). This indicates that ERSO could also act as a stabiliser in PVC compounds.

Mixing curves for compounds shown in Fig. 4 indicate that compound B has a lower stabilising torque compared to control compound A. But it has very low degradation stability time (35 min only) compared with other compounds. On partial replacement of DOP in compound B with ERSO (compounds C, D and E), the nature of the mixing curve becomes similar to that of the control, even though these compounds show a marginal increase in stabilising torque. There was no sign of degradation of these compounds even after 50 min of mixing at 170°C. Thus partial replacement of DOP with ERSO in compound B is helpful to enhance the overall performance of compound B. In the case of B, after 35 min, the torque increases to a maximum and then decreases. This is because the material breaks down to a powder under shear, after crosslinking.[12] The increase in toque at 35 min is because of the crosslinking of the resin followed by thermal degradation to black powdery material. Compound C contained stabilising system zinc oxide/magnesium oxide and stearic acid. But in compound D, the dosages of stabilisers magnesium oxide and stearic acid were lower and in E, magnesium oxide, zinc oxide and stearic acid dosages were only half of those in compounds B and C. Even then, these two compounds showed tensile properties similar to those of A, B and C, before and after aging at 100°C for 48 h (Table 6). In the case of compound D, a slightly higher tensile strength was obtained, which may be because of the presence of a higher dosage of zinc oxide, which is capable of reacting with the HCl eliminated during degradation of PVC. This indicates that use of ERSO in PVC compounds stabilised with the zinc oxide/magnesium oxide/stearic acid system, is helpful to enhance its thermal stability without adversely affecting its tensile properties. Compounds 1 and A are of the same composition, but showed a difference in tensile strength values. This is because a different grade (103 EP) of PVC was used for compounds A to E.

Effect of ERSO as heat stabiliser

From Table 5, it can be seen that for compounds 8 and 9, there is no change in stabilised torque for 50 min. Thus, it became evident that ERSO had heat stability. For compounds A, C, D and E also, there is no degradation for 50 min. But, for compound B degradation started at the 35th minute. These results indicate that ERSO could be used as a heat stabiliser for PVC, both in conventional type and modified compounds containing the MgO/ZnO/stearic acid combination. Since MgO/ZnO are rubber compounding ingredients, ERSO may be a useful additive in blends of PVC with elastomers.

Figure 7 shows the thermogram for compounds 1 and 2. For compound 2, the initial weight loss at a lower temperature is less than in compound 1. This is because of the higher molecular weight of ERSO, which is in the range of 960, compared with that of DOP, which is 390.[19] Degradation started first for the compound containing DOP alone.

From Fig. 9, it can be seen that compound 10, which does not contain TBLS, shows a regular change of colour from yellow to brown at early times compared with compound 8 that contained 50 parts DOP and 10 parts ERSO. The colour of the sample from compound 8 at the 60th minute is almost the same as that of the 25th minute sample of the compound containing DOP alone (compound 10). From this it is evident that the

50 : 10 DOP/ERSO combination gives a more stabilising effect than 60 parts DOP alone. The light yellow colour of compound 8 at the 3rd minute is due to the yellow colour of the ERSO. It is evident from Fig. 10 that the colour of compound B changed from white to brown within 35 min of mixing whereas compounds A, C, D and E did not change to brown even after 60 min mixing at 170°C. The light yellow shade of sample E is because of a higher dosage of ERSO, which is light yellow. These observations further supported the fact that ERSO can be used as a heat stabiliser for PVC.

Conclusion

The study showed that ERSO could be used as a secondary plasticiser for PVC. It gives heat stability for PVC and is less volatile. Compounds containing mixtures of ERSO and DOP had tensile properties comparable to that containing DOP alone. Reduction in amount of zinc oxide, magnesium oxide and stearic acid in the stabiliser system did not affect the thermal stability of PVC when a combination of DOP and ERSO is used as the plasticiser. The DOP/ERSO system works very well with ZnO/MgO in imparting thermal stability to PVC.

References

1. N. Nadaraja Pillai and R. T. Wijewantha: *Rubber Res. Inst. Ceylon Bull.*, 1967, **2**, 8–17.
2. G. Azeemoddin and S. D. Thirumala Rao: *Rubber Board Bull.*, 1962, **6**, 59–68.
3. K. Vijayagopalan: *Rubber Board Bull.*, 1971, **11**, 48–51.
4. K. Vijayagopalan and K. S. Gopalakrishnan: *Rubber Board Bull.*, 1971, **11**, 52–54.
5. A. I. Aigbodion: *Ind. J. Nat. Rubber Res.*, 1994, **7**, 141–143.
6. V. Haridasan: *Rubber Board Bull.*, 1971, **11**, 19–24.
7. A. I. Aigbodion: *Ind. J. Nat. Rubber Res.*, 1991, **4**, 114–117.
8. A. I. Aigbodion, A. R. R. Menon and C. K. S. Pillai: *J. Appl. Polym. Sci.*, 2000, **77**, 1413–1418.
9. A. S. Athalye and P. Trivedi: 'PVC technology, compounding, processing and application', 64; 1994, Bombay, Multi-Tech Publishing Company.
10. W. Sommer: in 'Plastic additives handbook', (ed. R. Gachter and H. Muller), 253; 1984, Vienna, Hauser Publishers.
11. V. R. Gowaricker, N. V. Viswanathan and J. Sreedhar: 'Polymer science', 237; 1986, New Delhi, New Age International (P) Ltd. Publishers.
12. L. I. Nass: in 'Encyclopaedia of PVC', Vol. 1, Ch. 8, 274; 1976, New York, Marcel Dekker.
13. V. R. Gowaricker, N. V. Viswanathan and J. Sreedhar: 'Polymer science', 271; 1986, New Delhi, New Age International (P) Ltd Publishers.
14. F. E. Okieimen and J. E. Ebhoaye: *J. Appl. Polym. Sci.*, 1993, **48**, 1853–1858.
15. F. E. Okieimen and J. E. Ebhoaye: *Angew. Makromol. Chem.*, 1993, **206**, 11–20.
16. F. E. Okieimen and J. E. Ebhoaye: *Eur. Polym. J.*, 1992, **28**, 1423–1425.
17. A. I. Vogel: 'Elementary practical organic chemistry', 2nd edn, Ch. 38, 825; 1958, London, English Language Book Society.
18. K. E. George, R. Joseph and D. J. Francis: *Plast. Rubber Process. Appl.*, 1985, **5**, 209–211.
19. J. K. Sears and J. R. Darby: 'The technology of plasticizers', 858; 1982, New York, John Wiley and Sons.