# Potential Application of ENR/EPDM Blends in the Dynamic and Endurance Conditions — A Review

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Since the process and conversion of natural rubber into epoxidized natural rubber (ENR) was discovered and patented by I. R. Gelling of the Malaysian Rubber Product Research Association (or now known as the Tun Razak laboratory), Brickendonbury, Hertford, in the United Kingdom, there are more than 10 000 technical and technological papers cited in the internet. Information on ENR is available, not only in the the English language but also other languages like Chinese, Malay, French, Thai and even German languages are used.

ENR is the most versatile and reactive rubber/elastomer. It is an advanced natural rubber which could be potentially used as a starting material for the development of other rubbers, modified elastomers, for grafting, plastic-based materials and also thermoplastic rubbers. Its reactivity is dependent on its epoxy groups, the opening of its ring structure, and also the subsequent structures of carboxylic groups and the *in-situ* side-chains "carbon – carbon" double bonds (> C = C <). In some instances, up to 65% epoxidation of NR is possible and achieved for more oil resistance. For these reasons, there are many new and advanced materials which have been formed and developed in the last two decades.

Among them, some of the recent research work is listed here. Apart from studies of compounding the ENR itself and its potential uses, there are many rubber-rubber blends and ENR rubber-plastics blends, some of the studies cited are "uses of new and advanced chemicals" and synthetic rubbers: ENR/NBR, ENR/PVC, ENR/polylactic acid blends, ENR/copolyester blends, ENR/Copolyamide Blends, ENR/poly (vinylidene fluoride) blends, ENR/Carbon Nanotubes with co-agent Trimethylol Propane Triacrylate, ENR /recycled silicon materials, and ENR/copolymer of *n*-butyl acrylate/butyl methacrylate "grafted". Each of these blends has its own characteristics in terms of processing, enhancement of processing like safety, scorch, oil and water resistance properties, or some in the development of potential thermoplastic rubber and its thermoplastic vulcanizates.

In this paper, the author would like to share some findings of the ENR/EPDM blends that have good flex and dynamic properties, relatively low compression set, and tolerant tensile properties that satisfy most rubber products that are required for and used in the industrial, mechanical, and even automotive parts. More importantly, the sliding skid resistance/frictional property and wear resistance of the blends are also examined. In some blends, the thermal dynamic behaviour is also measured over a temperature range depicting the low-temperature stability, its temperature of transition and the dynamic factor like tangent delta ( $\sigma$ ). These are the potential factors that could enhance the blend properties that give possible, good high speed and traction, applicable in tyres.

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The uniqueness of the epoxidised natural rubber (ENR) is that it is very reactive in terms of both nucleophilic substitution and free radical reactions, depending on the condition of a chemical reaction. Either it is its form or chemical modified, it is easy to process, and most of the common rubber chemicals can be used to plasticize and cure the rubber, and most of the rubber processing machine can be used. If it is thermoplastic form, then the common thermoplastic machines can be used too. In a more advanced state of the modified / grafted ENR, its surface can be cured or hardened by UV irradiation. This gives rise to the surface coating required for the protection of surfaces and also possibly used in the seal sector of the industry. At the low molecular level where the molecular weight is between 10 000 to 20 000 levels, it is used as a sealant and also used as a seal in the laminates.

In this paper, the author describes the results of the R&D in the ENR and ENR/ ethylene propylene diene monomer (EPDM) blends, especially at the 50:50 level, that has the potential applications in various industries. The vulcanization system is a mixture of low accelerated sulphur plus catalytic peroxide system that cure these blends, with the condensation reaction between the polymeric fractions with the in situ reactive chemical like organo-metallic titanate as reactant and compatibilizer that would assist in the incorporation of the non-carbon black fillers in the blends, and also enhances the grafting reaction of maleic anhydride onto the epoxides (in this case, the epoxidized NR). This uniqueness of this dual vulcanization system plus the coupling agent like organo-metallic

titanate with the incorporation of silica in the blends gives rise to a more holistic physical and thermal dynamic properties of the blended rubbers. This *in-situ* or in-process reaction, and sometimes, vulcanization, would result in developing strong bonds in the vulcanized modified blends.

The R&D work also describes how conventional tools like the resilient apparatus, pendulum slip and skid apparatus and phase control microscopic observation would be used to assess physical properties like abrasion, skid resistance, and the topological structures (by phase contrast microscopy) related to abrasion and wear surfaces, and the dynamic mechanical thermal analysis (DMTA) method for the study of compatibility and miscibility of the blends. All the methods of determination and testing are according to the testing standards and standard practices.

The epoxidation (Gelling 1984; Gelling & Smith 1979) though increases the polarity of the natural rubber (ENR), it also improves compatibility with the polar polymer. It also improves the properties of air impermeability, and substantially reduces oil-swelling. However, it still has good strength and retains its ability to strain-induced crystallization during stretching. Thus, it still behaves like NR. The ENR can be vulcanized by a typically accelerated sulphur curing systems. The epoxidation raises the glass transition temperature, thus reducing gas permeability and decreasing the lowtemperature resilience, leading to increased damping and making ENR-50 a highly damped rubber. However, at even higher temperatures

the high resilience of NR is maintained. Briefly, 25 and 50 mol% epoxidised natural rubber are produced and, which are marketed as ENR-25 and ENR-50. Despite the modification, ENR is still a strain-crystallizing rubber with high strength up to about 50% epoxidation.

In this paper, only the 50 mole% of the epoxidation on NR or known as ENR50 is used in the study. The epoxide groups are randomly distributed along the natural rubber molecule as shown below (*Figure 1*).

3. The use of the compatibilizer, organometallic titanate, and maleic anhydride in the final development of the blends in the dynamic and flex properties.

The physical properties of the blends tested were a tensile strength, Dunlop resilience, abrasion, the slide test, crescent tear, and dynamic flex.

In one series of the blends with and without fillers, the thermal dynamic mechanical properties of the blends were determined and



Figure 1. Epoxidized natural Rubber.

#### MATERIALS AND METHODS

# Preparation of the Blended Material and Testing

The blends of the ENR and EPDM in various ratios were mixed using a laboratory OOC Banbury, an intermixing of two litres, and then finally compounded on a two-roll mill, and cured to the optimum plus 2 min, after the test and assessment of the rheometer.

The series of development includes:

- 1. The unfilled and filled blends with calcium carbonate, silica and carbon black/silica
- To determine the compatibility and miscibility of blends by DMTA method; and

their glass transition behaviour and their relative tangent delta. The basic recipe and composition of the blends are recorded in the Figures or Tables in the results.

# The Dynamic Mechanical Thermal Analysis Properties of the Blends

The compatibility and miscibility of two rubbers in a blend are complex. Many methods are used to study these properties. One of the latest methods is the DMTA (*ASTM* 5992; *ASTM* E 1640) which measures thermal behaviour and stability of nature in the blends, especially the inter-physical morphologic structures and compatibility of the rubber phases in the blends could be studied. The study was carried over a range of temperature, and they were subjected to typical dynamic vibration of 10 Hz from  $-50^{\circ}$ C to 100°C, the temperature shift, the glass-transition temperature (*T*g) and the temperature peak of tangent delta (tan  $\sigma$  pk.) were measured). In this case, the properties of the blends (ENR 50/EPDM) with and without the fillers were studied.

# DMTA Properties of the Filled Compounds in ENR 50/EPDM Blends at 10 Hertz

The DMTA spectrum had two distinct regions /phase: the ENR 50 in the sub-zero phase, and EPDM phase at the higher temperature range. There were two glass transition temperatures; one in the ENR 50 phase and another in the EPDM phase, each with a maximum tangent delta. The results were of these blends, unfilled and filled with 40 phr calcium carbonate, and 40 phr silica. The results are shown in *Tables 1* (unfilled, gum-vulcanizates of blends; *Table 2* for

the vulcanizates filled with CaCO<sub>3</sub>; and *Table 3* for the vulcanizates filled with silica.

Except for the blends of the calcium carbonate filled for the EPDM phase, all the glass-transition temperatures, Tg, at each level of EPDM/ENR 50 ratio is similar, and independent of the type and nature of the fillers. For example, at the ratio of blend, EPDM 50% : ENR 50 50%, the Tg of the EPDM phase is 14.3°C for the gum-vulcanizate; 16.0°C for the silica filled; and in the ENR 50 rubber phase, the Tg is  $-34.9^{\circ}$ C for the gum, and -32.3 for the calcium carbonate filled, and -33.5°C for the silica filled respectively. It is interesting to note that the rest of the blends of the gum-vulcanizate and filled vulcanizates show similar trends at each ratio. This thermal, mechanical dynamic behaviour of the blends, that is, Tg, observed could be independent of the filler.

ENR 50	100	75	50	30	0				
EPDM	0	25	50	70	100				
Gum-vulcanized rubber	blends								
Hardness	43	43	46	47	52				
Dunlop resilience	24	28	32	38	63				
Τg°C	14.0	14.3	16.1	21.3	-				
Τg°C	-	-35.8	-34.9	-30.7	-27.0				
Tan σ pk (25°C)	1.903	1.421	1.036	0.478	-				
Tan $\sigma$ pk (25°C)	-	0.071	0.147	0.391	1.139				
Tan $\sigma$ pk (80°C)	0.081	0.078	0.097	0.119	0.10				
Accelerated sulphur cured blends									

CaCO <sub>3</sub> filled								
ENR 50	100	75	50	30	0			
EPDM	0	25	50	70	100			
Hardness	60	62	62	65	59			
Dunlop resilience	17	21	26	32	49			
Τg°C	7.6	6.9	5.6	4.6	-			
Τg°C	-	-35.2	-32.2	-30.0	-28			
Tan $\sigma$ (25°C)	1.0	0.733	0.575	0.416	-			
Tan $\sigma$ (25°C)	-	0.085	0.168	0.270	0.693			
Tan $\sigma$ pk (80°C)	0.081	0.078	0.097	0.119	0.100			
Accelerated sulphur cured blends								

Table 2. The DMTA properties of  $CaCO_3$ -filled.

Table 3. The DMTA properties of silica filled.

Silica filled								
ENR 50	100	75	50	30	0			
EPDM	0	25	50	70	100			
Hardness	70	75	76	72	67			
Dunlop resilience	20	24	29	34	56			
Τg°C	13.2	13.33	16.0	21.1	-			
Τg°C	-	- 34.6	- 33.5	- 32.3	-29.5			
Tan σ pk (25°C)	0.752	0.565	0.429	0.311	-			
Tan σ pk (25°C)	-	0.091	0.171	0.247	0.552			
Tan σ peak (80°C)	0.082	0.115	0.144	0.10	0.115			
Accelerated sulphur cured blends								

Portable Skid resistance tester results								
ENR 50%	0	20	35	50	80	100		
Dry terrazzo								
Skid No.	95	93	93	92	85	84		
Wet terrazzo								
Skid No.	19	20.2	21.0	22.0	23.5	25.0		
Oil terrazzo								
Skid No.	7	8	8.5	9	10	10.5		

Table 4. Portable skid resistance and friction.

However, the filler influenced the thermodynamic behaviour of the blend, especially the elastic moduli and the loss tangent (tan  $\sigma$  peak). The tan  $\sigma$  peak inclined to decrease as the amount of ENR 50 in the blends decreased, while at the same time, tan  $\sigma$  peak of the EPDM phase increased, as shown in Tables 1 (gum-vulcanizate), 2 (calcium carbonate filled), and 3 (silica filled). Then the DMTA was carried out at the temperature of 80°C, allowing the equilibrium period of 5 min, the scenarios changed. All the Tg's of the two phases collapsed and merged into a single phase, and only a single tan  $\sigma$  peak was observed. These tan  $\sigma$  peak values observed were much reduced in the range of 0.081 to 0.115. The silica series had marginally higher

values at each level of blends. Though the ENR 50 is more polar than natural rubber, it was not as compatible as it is was shown in the blends, and at 80°C, the thermodynamics of each blend was more homogeneous, and no double tangent delta peaks were observed.

#### The Physical Properties of the Blends

The tensile properties like strength (TS) and the elongation-at-break (EB) were affected by the blend ratios and, they are within the range of 15.7 to 19.2 MPa for the TS, and 530% to 610% for the EB respectively, and these data were within the specification and performance of most rubber products. The results are shown in *Figure 2*.



Figure 2. Tensile properties.

The other properties of the blends were also determined. They are the abrasion resistance in ml/per run of the Din abrasion tester and crescent tear in Newton/mm strip. These results are shown in Figure 3. The tear resistance as indicated by crescent type increased from 13.8 Newton/mm (100% EPDM) to 14.5 Newton/ mm at the 50% blend ratio, and decreased as the addition of ENR 50 to 7.4 Newton/mm in 100% ENR 50. Thus, the addition of the EDPM in the blends improves the abrasion resistance of the blend. The abrasion loss decreased as the addition of the ENR 50 in the blends. It decreased from 0.30 cc for the 100% EPDM, through 0.28 cc in the 50:50 ratio of the blend, to the lowest 0.23 cc in the 100% ENR 5, which correlated well with the tear behaviour of the blends. The abraded surfaces of these blends were examined under microscopy, and the results of the micro-structures and possible voids are shown in the next few Figures.

# Skid Resistance and Equivalent Friction of the Blends

The contact behaviour like skid resistance of a rubber surface is complex and hard to determine. One of the methods used is the portal skid resistance tester that is established in Britain, and commonly used to test road surfaces for the

assessment of risk at the site where accidents frequently occurred (ASTM E 303-1974). The tester was used to assess the skid resistance of a series of blends using a non-bitumen tar surface, such as terrazzo which had more control over the surface nature. The dry, wet and oily surfaces were tested, and the relative skid resistance number were recorded, the equivalent fraction resistance was also computed, and the results are reported in Table 4. At the dry condition of the terrazzo, the difference in the skid resistance in the blends was marginal and small. The skid number recorded was relatively high even when they were determined using the dry, smooth terrazzo. As indicated by Giles et al. (1965) any skid number above 65 is considered 'good' fulfilling the traffic requirement of the road surface. However, for the wet condition, or the oily surface, the addition of the ENR 50 improves moderately in the wet skid resistance or its skid numbers are within the range of 19 to 25, which is classified as 'unsatisfactory', and similar range was reported by Sabey & Lupton (1964) for their work on wet smooth highly polished surface. Even more so in the oily surfaces, that is, from skid number 7 for the 100% ENR 50. The addition of the ENR 50 could generally improve the skid resistance on both wet and oily surfaces.



Figure 3. Abrasion, tear and flex.

## **Abraded Surface of the Blends**

The abraded surfaces of each blend was examined using a simple light microscopy and with a suitable range of magnification, the micro-structures of the surfaces was examined and photographed. The photographic images are shown in *Figures* 4 - 9. From the topographic images, there were voids or empty interphase spaces observed, and the spatial area increased as the ENR 50 decreased. The ridges (Bhomwick 1964), and depth of the voids were



Figure 4. Topography of 1000% EPDM.



Figure 6. Topography of 65% EPDM.

measured and average values computed, and the final equivalent volume of voids were plotted as shown in *Figure 10*. The volume of the void in the blends of various ratios increased as the percentage of ENR 50 increased. The volume and its distribution would affect the physical property, especially the abrasion, or even tear resistance. The occurrence of the voids is also observed by Loh and See Toh (1985) in their work on the electron microscopic study of the epoxidation of NR latex particles.



Figure 5. Topography of 80% EPDM.



Figure 7. Topography of 50% EPDM.



Figure 8. Topography of 20% EPDM.



Figure 9. Topography of 0% EPDM.



Figure 10. Void volume and surface area of abraded surface of the EPDM/ENR 50 blends.

# Improvement in the Morphology of Blends and in the Homogeneity of the Fillers in the Rubber Matrice

The above results and observations showed some discrepancies in the physical properties due to the heterogeneity of the blends. Of course, it was possible to have a better and more homogeneity of the blends, that is, to extend the time of mixing, time of incorporation of fillers and finally extending to the final homogenization, or to increase the temperature of mixing process. These either conditions would affect the flow and scorch behaviour of the final blend compounds, and also finally their physical properties and performance. To overcome these conditions, the organo-metallic titanates, and zirconates which are reactants and compatibilizers are sought, and they are widely used in the rubber compounds of chloroprene (neoprene), nitrile, butyl, hypalon, and others especially with non-black fillers. They are also effective for the dispersion and incorporation of non-black fillers; they are also effective for

the dispersion and incorporation of non-black fillers, like silica, lead oxides, and talc.

In this case, LICA38 (Monte et al. 1990), a neoalkoxy titanate in liquid form, is used for easy incorporation in the blends. It helps to not only compatibilize the rubber phases of the ENR 50 and EPDM, and also to assist in the homogeneous incorporation of silica in the rubber matrix. In this series, a combined carbon black and silica is used with a low sulphur semiefficient sulphur vulcanization system chosen, and be combined with a peroxide and maleic anhydride. They were mixed, compounded in the usual method using the Banbury where the maleic anhydride was added, and the active accelerators, sulphur, peroxide and titanate were added as usual on the mill. They were cured to the optimum, plus 3 min at 160°C.

The results in *Table 5* showed a great duel of improvement in terms of tensile properties. The abrasion and especially the compression

Black/silica filled-Fatigue/flex property of blends					ENR 50	0	70	50	25	100	
ENR 50	0	70	50	25	100	EPDM	100	25	50	75	0
EPDM	100	25	50	75	0	Hardness	69	65	77	69	62
Hardness	69	65	77	69	63	Dunlop resilience	64	45.7	36.7	29.0	28.0
Dunlop resilience	64	45.7	36.7	29.0	28	40°C	64.5	47.6	42.3	35.3	36.0
TS, MPa	28.2	18.9	17.2	16.8	15.3	60°C	60.5	57.1	50.7	44.8	45.7
EB, %	680	590	580	530	510	80°C	62.4	59.3	52.7	48.5	48.5
Compression set						Aged properties					
22 h/70°C	24.3	28	27.5	25.6	28	70 h/100°C					
22 h/100°C	37.6	41.7	43.1	46.7	60.1	TS ret. %	93	90	90	86	76
Abrasion	52.3	74.4	83.3	92.0	101.0	EB, ret %	83	85	71	69	67
Crescent tear,	Crescent tear,		70 h/125°C								
N/mm	41.8	46.8	35.6	27.5	16.2	TS ret. %	82	80	79	83	71
						EB ret. %	81	76	49	25	28
De Matia flex	De Matia flex										
Kilocycle × 10 <sup>6</sup>	Kilocycle × 10 <sup>6</sup> 2.0 2.00 1.30 0.38 0.18										

Table 5. Effects of organ-metallic and maleic Anhydride.

set, even at 10°C, was still within 60%, and the retention of the tensile properties were relatively, at the conditions of 70 h/125°C. The high level of ENR 50 in the blends had lower tensile and abrasion resistance properties. The resilience property related to the hysteresis of the blends measured at 40°C, 60°C, and even 80°C were high, indicating possibly that the rolling resistance which should be possibly and relatively high too. The results of dynamic flex properties determined by de Matia flexing machine were very high, in terms of more million kilocycles. Normal natural rubber compound would have 150-300 kilocycles. The overall observations in this final series of blends were that the addition and incorporation of the maleic anhydride in the polymer phase during mixing and the titanate as the compatibilizer and coupling agent in these blends enhanced the physical properties, abrasion and tear resistances, and compression set plus the endurance/flex properties. This improvement in the blends, especially at the levels of 25% or 50% of ENR 50 in the EPDM compounds will be ideal for high endurance and performance applications such as in tyre, and for the lower end-applications, the non-slide shoe soles application on wet ship decks, and the seminiche market applications in the high speed cycle tyres as discussed by Loh and See Toh (1988) on the ENR in tubeless inner liners.

# Chemical Reaction Mechanism that Possibly Enhances the Properties of Vulcanizates of the Blends

The possibility of chemical mechanism that leads to the overall balanced and enhancement of the physical, dynamic and abrasion properties is the participation of the maleic anhydride in the vulcanisation and also in situ dynamic situation. Though the maleic anhydride is purported and mechanistically favoured an Diels-Alder reaction (Alder et al. 1943) in the methylene/allylic double carbon bonds (>C = C<) as reported in the classical chemical reactions (Baraboim & Popov 1963), and also by Pinazzi (Pinazzi et al. 1963), and Farmer (1942)in natural rubber, while Loo (1985) reported that it is possible that the dibasic acids could be used to open the epoxide ring and also used as crosslink sites, or the dibasic acids used to crosslink in the non-sulphur accelerated curing system.

In this present scenario, apart from the chemical reaction in the methylene/allylic sites, it was possible that the chemical reaction mechanism could occur where the maleic anhydride reactd with the epoxy group to form a carboxylic group and reacted with another to form an effective crosslink (*Scheme 1*), both



Scheme 1. Reaction by substituting.

through the normal substituting reaction, or the free radical reaction in the presence of a peroxide as proposed below (*Scheme 2*). These "maleic anhydride crosslinks" being more flexible than the normal sulphide crosslinks (mono- and disulphides types) and would enhance dynamic property like flexing and endurance. Coupled

with the low sulphur accelerator curing system, the vulcanized blends could have achieved its ultimate and optimal properties, and the performance using this type of curing system would enhance the overall physical, abrasion resistance and dynamic performance.



Scheme 2. Possible reaction of maleic anhydride in a free radical reaction mechanism.

#### SUMMARY

The physical properties due the heterogeneity of the blends of the ENR 50 and EPDM were in question, even though the ENR was more polar than normal NR. Of course, it was possible to have a better, and more homogeneity at each of the blends was to extend the time of mixing, time of incorporation of fillers and finally extending to the final homogenization, or to increase the temperature of the mixing process. Either of the conditions would affect the flow behaviour and scorch of the final blend compounds, and also finally, in turn, affect their physical properties and performance. To overcome these conditions, the LICA38 (Monte 1999), a neoalkoxy titanate in liquid form is used in the blends. It enhanced compatibilization of the rubber phases of the ENR 50 and EPDM, and also to assist in the most homogeneous incorporation of silica in the rubber matrix and rubber phases. The dispersion of the combined carbon black and silica was more homogeneous as shown by the results. With a low sulphur accelerated semi-efficient vulcanization system chosen, plus a combination with peroxide and maleic anhydride the crosslinked blended through the epoxide groups and showed excellent physical and performance properties like abrasion and tear resistance. The dispersion of the combined carbon black and silica was more homogeneous as shown by the results. With a low sulphur accelerated semi-efficient vulcanization system chosen, plus a combination with peroxide and maleic anhydride the crosslinked blends showed excellent physical and performance properties like abrasion and tear resistance.

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#### APPENDIX

# For *Figures* 1 – 10:

ENR 50, EPDM (Exxon7000), Stearic acid 2, Sulphur 1.5, CBS 1.0, TMTD 0.1, TMQ 1.2, CaCO<sub>3</sub> 30 phr , silica 25 phr filled blends, DEG 5.

# For Table 1:

ENR 50, EPDM (#4050), ZnO 5.0, Stearic acid 2.0, Sulphur 1.5, CBS 1.0, TMDT 0.5, TMQ 1.2

#### For *Table 2*:

EPDM (#4050), ZnO 5.0, Stearic acid 2.0, Sulphur 1,5. CBS 1.0, TMDT 0.5, TMQ 1.2, CaCO<sub>3</sub> (30 phr) filled blends, blends.

## For *Table 3*:

EPDM (#4050), ZnO 5.0, Stearic acid 2.0, Sulphur 1.5, CBS 1.0, TMDT 0.5, TMQ 1.2, silica (30 phr) filled blends, DEG 1.2.

# For Table 4:

ENR 50, EPDM (#4050), Stearic acid 2, Sulphur 1.5, CBS 1.0, TMTD 0.1, TMQ 1.2, CaCO<sub>3</sub> 30 phr, silica 25 phr filled blends, DEG 5.

#### For Table 5:

ENR 50, EPDM (Exxon 7000), Stearic acid 2, Sulphur 1.5, CBS 1.0, TMTD 0.1, TMQ 1.2, carbon

black 20 phr, silica 35 phr filled blends, DEG 5, LICA38, anhydride 0.25 and DiCup $\mathbb{R}$  R 1.0 and ZMB2 1.0

CBS N-cyclohexyl 2-benzothiazyl suplhenamide

TMTD Tetramethyl thiuram tetrasuphide

TMQ polymerised 2.2.4-trimethyl1, 2 hydoquiline

DE G diethylene glycol

LICA 38 neoalkoxy titanate, patents, Kenrich Group

ENR 50 Guthrie's Group of Company / RRIM

Exxon 7000 Exxon Goup

# EPDM from Japan

Dicup® R, dicumyl peroxide