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Rolling-ball Rubber-layer Isolators[†]

A.H. MUHR^{*#}, M. SULONG^{*} AND A.G. THOMAS^{**}

A system has been developed for seismic isolation of light structures, with no restriction as to choice of deflection capacity, damping or period. It comprises: isolators consisting of balls rolling between tracks; damping provided by layers of dissipative material, such as rubber, bonded to the tracks and hence integral with the isolators; separate springs to provide a restoring force.

The use of rubber layers to provide rolling resistance permits a very wide choice of effective damping level, and the rolling resistance can easily be arranged to be a preset function of displacement. The design of the isolators is thus more versatile than for sliding isolators, which are otherwise similar in concept.

Experimental results are presented for the steady rolling resistance as a function of load, ball radius, rubber thickness, rubber nature and rolling velocity. The peak in horizontal force required to start the balls rolling depends on the length of time for which the load is applied before rolling starts as well as on the above parameters. This peak in force could be beneficial in providing resistance to wind loads, but if too high could prevent the isolation system operating in an earthquake.

It is difficult to design economical laminated rubber isolators that support light structures and achieve values of horizontal period and deflection capacity required by seismic isolation systems. These required values are much the same whatever the weight of the isolated structure, with the deflection capacity being controlled mainly by the plan dimension of the bearings¹ while the period T is given by:

$$T = 2\pi \sqrt{\frac{M}{K}} \quad \dots 1$$

where M is the mass of the isolated structure and K is the combined horizontal stiffness of the bearings. Thus, for a low value of M we must design bearings of low stiffness. This is difficult to reconcile with keeping their width constant¹, since to make the stiffness low we need either to make the bearings very high, with a lot of laminations to maintain stability, or to construct a composite bearing by linking together an array of bearings of reduced width with plates at several intermediate heights, again to control stability². As well as making design difficult, such bearings will be costly to make.

[†] Paper presented at the International Rubber Conference 1997 Malaysia, 6-9 October, Kuala Lumpur

^{*} Tun Abdul Razak Research Centre, Brickendonbury, Hertford SG13 8NL, United Kingdom

^{**} Materials Department, Queen Mary and Westfield College, University of London, London E1 4NS, United Kingdom

[#] Corresponding author

ห้องสมุดพระมณฑลวิทยาศาสตร์บริการ
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The problem with using laminated bearings for light structures arises from the combination of the spring and isolator functions. A system has been developed³ which separates these functions and hence enables isolation of even very light structures, with no restriction as to the choice of deflection capacity, damping or period. It comprises:

- Isolators consisting of balls rolling between tracks
- Damping provided by layers of dissipative material, such as rubber, bonded to the tracks and hence integral with the isolators
- Separate springs to provide a restoring force.

The use of rubber layers to provide rolling resistance permits a very wide choice of effective damping level by choosing layers of different thickness (zero thickness giving zero damping) and compounds with different levels of hysteresis. The rolling resistance can easily be arranged to be a preset function of displacement by varying the thickness and/or the rubber formulation (and hence hysteresis) with distance along the rolling path. The design of the isolators is thus more versatile than for sliding isolators, which are otherwise similar in concept.

The basic force-displacement characteristic of the rolling-ball isolation system is shown in *Figure 1*. The slope of the hysteresis loop gives the stiffness K which determines the period T of the system (*Equation 1*) while the area of the loop, proportional to the rolling resistance F_R , controls the damping coefficient of the system.

This paper is concerned only with the rolling resistance, and how it is influenced by the choice of rubber, its thickness, the load on the ball and the radius of the ball.

THEORY

Relationship of Rolling Friction to Indentation Work and Hysteresis

We define the frictional force Q as the work done when the ball rolls a unit distance on a single viscoelastic track. *Figure 2* shows possible schemes for measuring Q . According to Gent and Henry⁴, the work of indentation U is in effect applied and relaxed $1/2a$ times in unit rolling distance, where a is the contact radius; thus, if we assume a fraction α of the indentation is lost on each cycle we have:

$$Q \approx \alpha U/2a \quad \dots 2$$

The friction ratio μ is given by:

$$\mu = Q/W \approx \alpha U/2aW \quad \dots 3$$

Theoretical Equation for Rolling Friction for an Infinitely Thick Layer

According to Hertz the contact radius a and indentation depth d for an elastic half space of Young's modulus E are given by⁵:

$$a = \left[\frac{3}{4} WR \left(\frac{1 - \nu^2}{E} \right) \right]^{\frac{1}{3}} = \left[\frac{9}{16} \frac{WR}{E} \right]^{\frac{1}{3}} \quad \dots 4$$

$$d = a^2 R = \left[\frac{9}{16} \right]^{\frac{2}{3}} \left[\frac{W}{E^2 R} \right]^{\frac{1}{3}} \quad \dots 5$$

where Poisson's ratio ν has been set to the value for rubber, 0.5. The indentation work may be calculated from *Equation 5*:

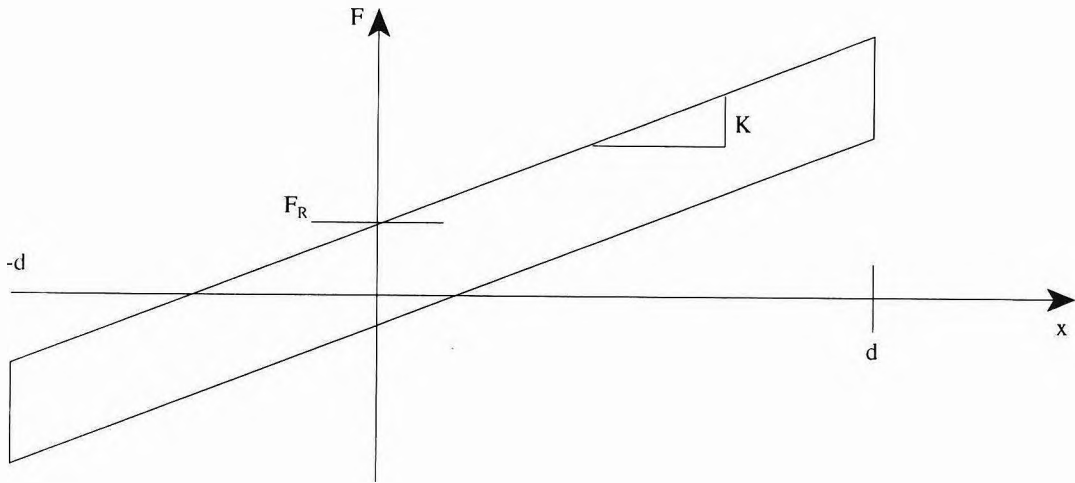


Figure 1. Schematic hysteresis loop for isolation system consisting of rolling-ball isolators and springs.

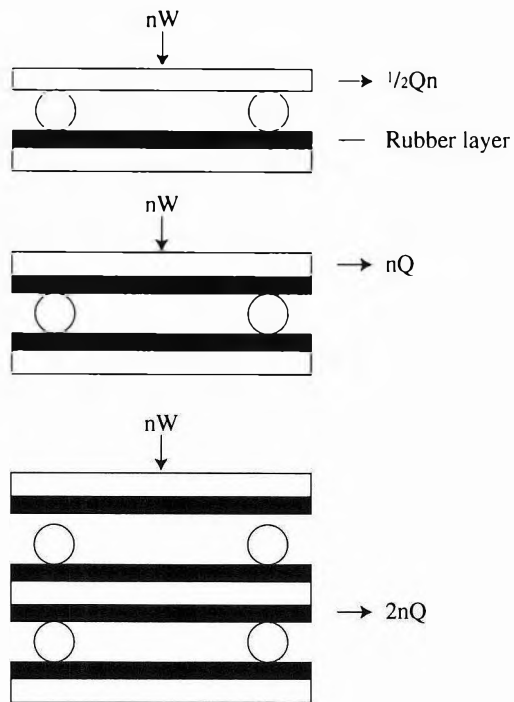


Figure 2. Possible arrangements of balls and rubber layers for isolators or for experimental determination of rolling resistance; n is the number of balls in one layer.

$$\begin{aligned}
 U &= \int_0^d W dx = \frac{16}{9} ER^{\frac{1}{2}} \int_0^d x^{\frac{3}{2}} dx \\
 &= \frac{2}{5} \cdot \frac{16}{9} ER^{\frac{1}{2}} d^{\frac{5}{2}} \\
 &= \frac{2}{5} \left[\frac{9}{16} \right]^{\frac{2}{3}} \left[\frac{W^5}{E^2} R \right]^{\frac{1}{3}} \quad \dots 6
 \end{aligned}$$

Combining *Equations 3, 4 and 6* we find:

$$\begin{aligned}
 \mu_{\infty} &\cong \frac{1}{5} \left[\frac{9}{16} \right]^{\frac{1}{3}} \left[\frac{W}{ER^2} \right]^{\frac{1}{3}} \alpha \\
 &\cong 0.165 \left[\frac{W}{ER^2} \right]^{\frac{1}{3}} \alpha \quad \dots 7
 \end{aligned}$$

where the subscript ∞ refers to an infinitely thick layer. *Equation 7* has been proposed in several publications albeit with different values for the numerical coefficient, as reviewed by Gent and Henry⁴.

Theoretical Equation for a Layer of Finite Thickness

Waters⁶ carried out an experimental investigation of the effect of rubber layer thickness on the indentation. His experiments covered the regime of small loads and indentations for which it may be reasonable to assume that a and d are related to each other in the same way as in the Hertz theory (see *Equation 5*):

$$a \cong \sqrt{dR} \quad \dots 8$$

and d is modified from the Hertzian value d_{∞} at $t = \infty$ (given by *Equation 5*) according to:

$$d = d_{\infty} f(t/a) \quad \dots 9a$$

where the function $f(t/a)$ was determined empirically as:

$$f(t/a) \cong 1 - \exp(-At/a) \quad \dots 9b$$

where A has the values 0.417 and 0.67, respectively for bonded and lubricated boundary conditions at the back of the rubber sheet.

To calculate the indentation work we need to express W in terms of d . Substituting *Equation 5* for d_{∞} as a function of W , and *Equation 8* for a as a function of d , into *Equation 9* we find:

$$\begin{aligned}
 W &= \left[\frac{d}{f(t/\sqrt{Rd})} \right]^{\frac{3}{2}} ER^{\frac{1}{2}} \frac{16}{9} \\
 &= (Et^3/R)(16/9)g(s) \quad \dots 10
 \end{aligned}$$

where $g(s) = [(s^2/f(s^{-1}))^2]^{\frac{3}{2}}$ and $s = \sqrt{(Rd)}/t$. Rearrangement of *Equation 10* would enable E to be calculated from s (and hence d). Inversion of the equation shows that s is a function of the non-dimensional group (WR/Et^3) .

$$\begin{aligned}
 \text{Thus } U &= \int_0^d W dx \\
 &= (Et^3/R)(16/9) (2t^2/R) \int_0^s g(s) s ds
 \end{aligned}$$

If we write the integral as $I(S)$ we see that:

$$U = (Et^5/R^2) (32/9) I(S) \quad \dots 11a$$

From *Equation 9* we see that $1/f(s^{-1})$ is unity at $s = 0$ and rises monotonically as s increases. It may be deduced that:

$$S^5/5 < I(S) < (S^5/5)[f(S^{-1})]^{-3/2} \quad \dots 11b$$

If we substitute *Equation 11a* into *Equation 3* and express a in terms of d using *Equation 8* we find an expression for μ as a function of d :

$$\begin{aligned} \mu &= \frac{\alpha}{2W} d^{-1/2} R^{-1/2} (E t^3 / R^2) (32/9) I(S) \\ &= \alpha (16/9) (E t^3 / R^2 W) S^{-1} I(S) \\ &= \alpha (16/9) (W / R^2 E)^{1/3} (E t^3 / WR)^{4/3} S^{-1} I(S). \end{aligned}$$

Using *Equation 7* to express $\alpha(W/ER^2)^{1/3}$ in terms of the rolling friction ratio μ_∞ for a semi-infinite layer and *Equation 10* to express $(E t^3 / WR)$ in terms of S we find finally that:

$$\mu = \mu_\infty \cdot 5 [f(S^{-1})]^2 S^{-5} I(S) \equiv \mu_\infty \Phi(S) \dots 12a$$

The non-dimensional quantity Φ , a function of RW/Et^3 , should tend to unity as $W \rightarrow 0$ or $t \rightarrow \infty$ and to zero as $t \rightarrow 0$. From inequality (*Equation 11b*) we may further deduce that:

$$[f(S^{-1})]^2 < \Phi < [f(S^{-1})]^{1/2} \dots 12b$$

The predictions of the theory are presented in the dimensionless plot of *Figure 3*. The ordinate μ/μ_∞ , is equal to $\Phi(S)$ from *Equation 12*, and is calculated using *Equations 9, 11* and *12* by numerical integration, making use of the bounds (*Equation 11a* and *Equation 12a*) to make sure the results are sensible when s is small. The abscissa $(t/R)/(W/ER^2)$, is equal to $[(16/9) g(S)]^{-1/3}$ from *Equation 10* and is calculated using *Equation 9*. To construct the plot, the parameter s is varied over a sufficiently wide range.

From *Figure 3* the theory predicts that the Hertzian theory is applicable when

$$(t/R) \geq 10(W/ER^2) \dots 13$$

Scaling Rules and Dimensional Analysis

It is desirable to identify scaling rules, so that experiments carried out on one scale may be used to predict the value of μ at other scales. If linear dimensions are scaled by λ , we have:

$$\begin{aligned} \text{Ball radius } R &\rightarrow \lambda R \\ \text{Rubber thickness } t &\rightarrow \lambda t \end{aligned} \dots 14a$$

It follows that to keep the stresses the same (and hence all dimensionless quantities such as strains and angles) the load W must be scaled by λ^2 :

$$\text{Load } W \rightarrow \lambda^2 W \dots 14b$$

Being dimensionless, the friction ratio μ should be unaltered if W is scaled as in *Equation 14b*. Because the hysteretic factor α may depend on rate the rolling velocity v should, strictly, also be scaled so as to keep the frequency $v/2a$ constant:

$$\text{Velocity } v \rightarrow \lambda v \dots 14c$$

It follows from *Equation 14a* and *Equation 14b* that for one rubber at one rate μ must depend only on W/R^2 and t/R . If, furthermore, the rubber properties enter only through the parameters E and α , it should be possible to construct master plots of μ/α versus t/R with W/ER^2 as the parameter. Examples of such plots, based on the theory given above for layers of finite thickness and low loads, are given in *Figure 4*. This figure is derived from *Figure 3* by multiplying both the ordinate and the abscissa values by $(W/ER^2)^{1/3}$. Based on the literature, reviewed by Gent and Henry⁴, we would expect the theory to be satisfactory provided W/E^2R is sufficiently low. Although the shape of the graphs at high normalised stress

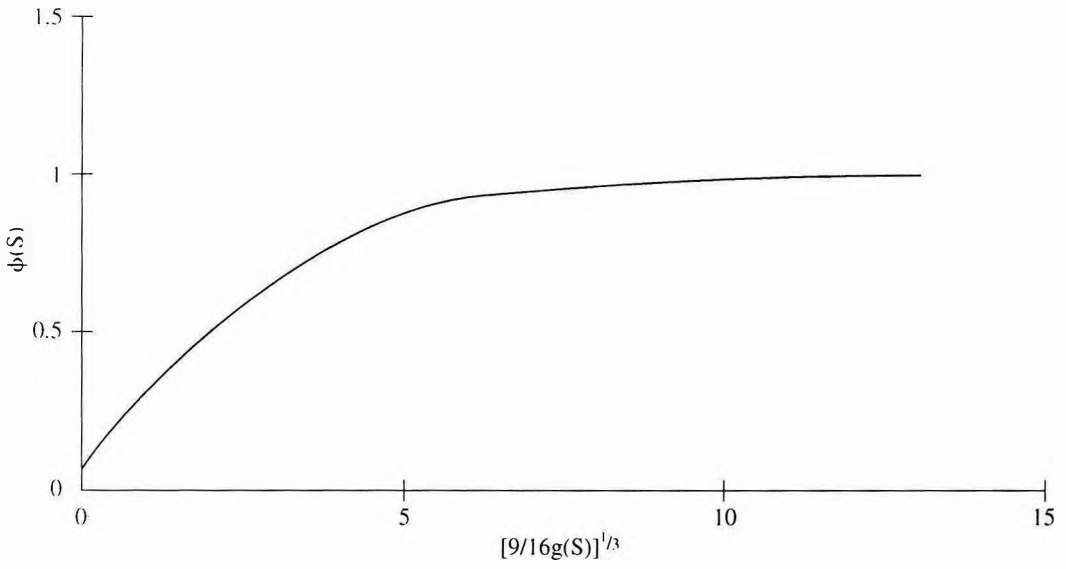


Figure 3. Theoretical plot of reduced friction ratio versus reduced rubber thickness (Equation 12).

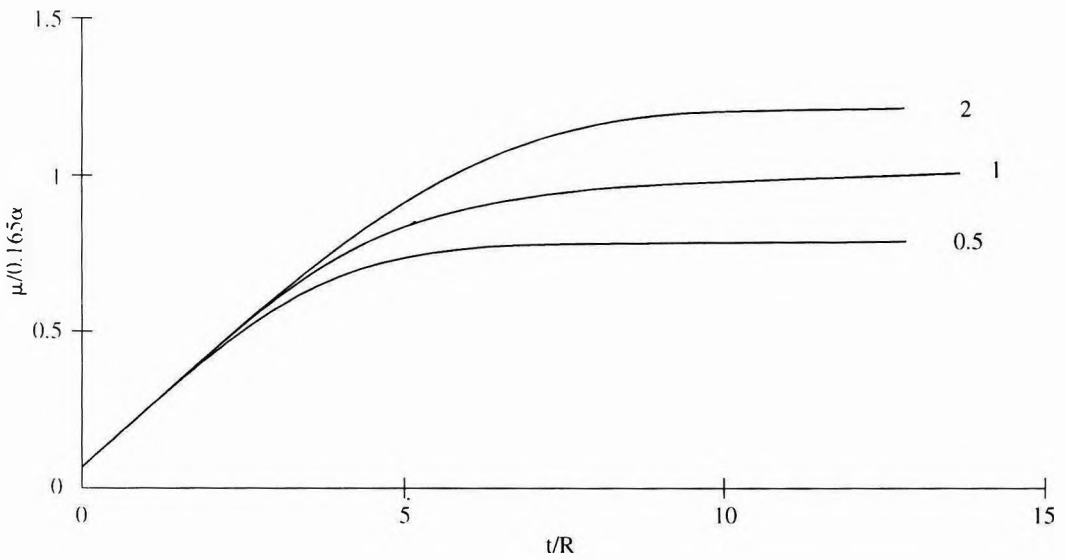


Figure 4. Theoretical plots of friction ratio μ , scaled using hysteresis parameter α , versus ratio of rubber layer thickness t to ball radius R [Equations (12) and (7)]. Parameter is W/ER^2 .

may not collapse onto the single plot of *Figure 3*, it should be possible to present them in the manner of *Figure 4*, albeit with shapes diverging from the theoretical plots when W/ER^2 is large.

EXPERIMENTS

Materials and Testpieces

The formulations, standard physical properties and dynamic shear properties of the rubbers used are given in *Table 1*.

The rubber was bonded to steel rolling plates (74×145×12 mm) in layers of various thicknesses. The rubber surfaces were moulded against *Mylar* (polyester film) to produce a good, smooth, surface profile and to keep it clean. Bonding was achieved during vulcanisation using *Chemlok 220*, either directly to the rolling plates or (for earlier testpieces) to 0.1 mm thick aluminium foil which was subsequently stuck to the rolling plates using double-sided adhesive tape.

Unless otherwise stated the surface of the rubber layers, on which the balls were rolled, were dusted with talc.

Method and Procedure

The experimental arrangement is shown in *Figure 5*. In all cases, a set of four balls was used between the rolling plates, the crosshead speed was 1 mm min⁻¹ and the temperature was 23±2°C. The rolling unit was connected to the load cell and crosshead of the Instron machine by nylon-coated multistrand wire. The coated wire was hooked to the top rolling plate, passed through the pulley and fixed securely by the pin of the load cell. The apparent

stiffness of the pulling cable, measured using the same load cell and crosshead arrangement, was 13 Nmm⁻¹. Also the horizontal and vertical alignments of the wire were adjusted visually so that they always remained parallel to the centre of the balls (*i.e.* rolling unit) and crosshead (load cell) of the machine, respectively, when the top plate with the mass moved forward. The load cell and cross head position outputs were connected to an XY recorder.

When the crosshead of the Instron machine travels upwards, it pulls the cable. Since the cable was hooked to the rolling unit the tension rises until the top rolling plate starts to move forward. This leads to a peak in the force as shown in *Figure 6*. The tension then falls to a minimum, perhaps enhanced by the tendency of the mass (once accelerated) to travel under its momentum. This occurs for a very short time, before a steady rolling speed is achieved (*i.e.* steady state rolling frictional force). One disadvantage of this technique is the difficulty of obtaining a straight rolling path particularly for low rolling friction conditions such as for a low normal load, with highly resilient talced rubber.

In order to check the reliability of the technique, a separate experiment was carried out using steel balls (3.175 mm radius) but no rubber layer. All other parameters remained the same except the normal load was applied starting from zero and the balls were rolled either directly on the steel plate or on the aluminium sheet alone which was held to the rolling plate by double-sided adhesive tape. When the Instron crosshead was run at 1 mms⁻¹ with no mechanical connection between load cell and the roller assembly, the electrical noise in the load cell output, as measured on the xy

TABLE 1. FORMULATIONS OF THE RUBBER COMPOUND USED IN THE EXPERIMENT

Ingredients	No. 1 (p.p.h.r.)	No. 3 (p.p.h.r.)	No. 4 (p.p.h.r.)
Natural rubber (SMR CV60)	100	100	
NBR (<i>Breon N41C80</i>)			100
Zinc oxide	5	5	5
Stearic acid	2	2	2
<i>Santoflex 13</i>	3	3	1
<i>Antilux 600</i>	3	3	–
Curatives:			
Sulphur	1	0.6	2.5
CBS	0.75	0.45	0.5
Cure time (min)	50	50	45
Cure temp. (°C)	140	140	150
Hardness (IRHD)	34	28	51
Tensile properties:			
M100 (MPa)	0.60	0.42	1.19
TS (MPa)	15.1	6.70	14.7
EB (%)	702	974	565
Lupke rebound resilience (%)	80.1	73.9	19.7
Dynamic properties 50% strain, 0.01 Hz:			
G (MPa)	0.32	0.24	0.72
δ (°)	1.3	3.0	5.3
50% strain, 0.1 Hz:			
G (MPa)	0.33	0.26	0.81
δ (°)	1.4	3.8	6.7
50% strain, 1 Hz:			
G (MPa)	1.34	0.28	0.94
δ (°)	2.2	4.9	7.9

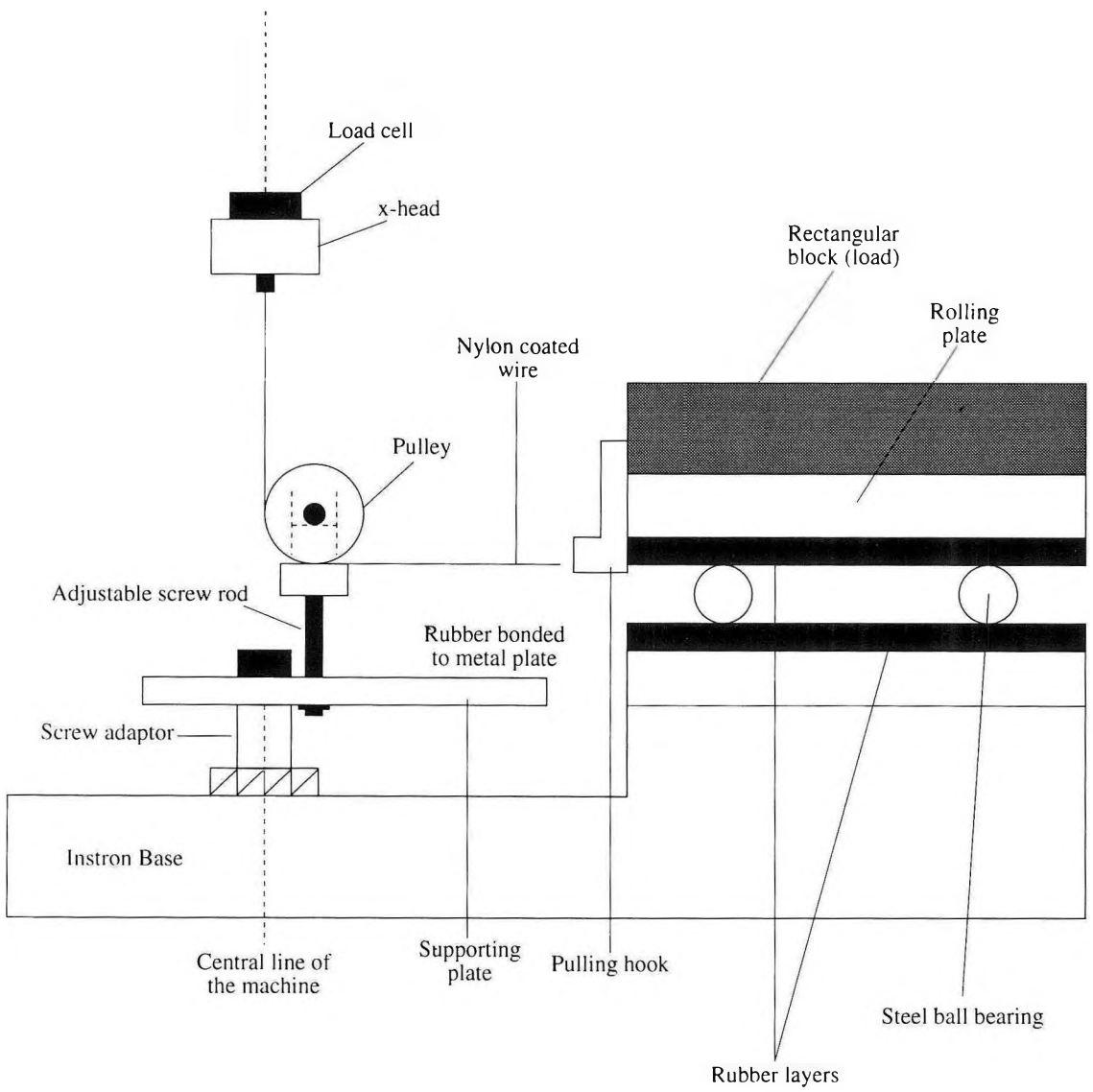


Figure 5. Apparatus for measuring rolling forces.

chart recorder, corresponded to 0.0015 N (peak to peak). In the case of rolling directly on the steel, the plate does not roll smoothly or in line with the pulling direction because of the machining marks on its surface. The peaks in horizontal force are about 0.2 N for a total normal load of 10 N. If the steel plates were replaced with glass plates it was not possible to level sufficiently accurately to prevent spontaneous rolling, while peak forces of only about 0.03 N for a load of 46 N were recorded. It was found that with aluminium sheet bonded to the steel the results were consistent with a steady rolling friction coefficient of about 0.06 and a peak roll-out value about 30% higher for total normal loads in the range 10 N–72 N. Because this value is rather high, the use of the aluminium backing foil (and double-sided tape) was abandoned for later experiments; instead the rubber layers were bonded directly to the steel backing plates using *Chemlok 220*.

RESULTS

Effect of Load and Rubber Thickness

A lightly crosslinked unfilled NR compound was used for these tests (No.3, *Table 1*). Layers of this rubber were bonded directly to rigid steel plates during vulcanisation. Nine thicknesses, ranging from 0.254 mm to 3.70 mm, were used. Balls of the following radii were used: 1.58, 2.0, 2.5, 3.0, 3.175, 3.5, 3.76, 4.0, 5.0, 6.0 and 6.25 mm. When the ball size was changed the load W per ball was also changed in such a way that the stress parameter W/R^2 was held constant over the range of t/R values investigated. Three levels of applied stress were used, corresponding to $W/R^2 = 1.0, 2.0$ and 5.2 MPa.

The steady-state rolling resistance results for $W/R^2 = 1$ MPa are given in *Figure 7*. The

results collapse onto a single curve, regardless of scale. This shows that the scaling rule works, despite the cross-head speed being kept constant at 1 mms^{-1} . Presumably the effect of rate is very weak. *Figure 8* includes results for the higher values of W/R^2 as well. The steady state rolling frictional coefficient rises as the thickness of the rubber layer is increased and tends to plateau.

A comparison was made between the plateau value of μ and the theory for a semi-infinite layer (*Equation 7*). The hysteresis parameter was calculated as $\alpha = \pi \sin\delta = 0.208$ from dynamic test results at 0.1 Hz and 50% strain (*Table 1*). The plot of μ_{plateau} against $0.165 (W/ER^2)^{1/3} \alpha$ is shown in *Figure 9*. At the lower loads there is fair agreement with the theory, although the dependence on load seems to be stronger than predicted so that at the highest load μ_{plateau} is 35% higher than predicted. The results also conflict with the extension of the theory to rubber layers of finite thickness, since the plateau region seems to be reached at quite low values of t/R , and the results are strongly dependent on the value of W/R^2 even before the plateaux are reached (cf. *Figure 4*).

These departures from the theory may well be a consequence of the high values of W/ER^2 being used, making predictions based on infinitesimal strain theory invalid. Indeed, for the largest of the stresses used ($W/R^2 = 5.2$ MPa) a permanent rolling track remained on the surface when $t/R < 0.55$. The rolling track is deep, almost reaching the backing plate in the case of the thinner rubber layers so that the blackness of the *Chemlok 220* layer could be seen through the very thin layer of rubber remaining. Obviously, the strains associated with such permanent tracks must be very large.

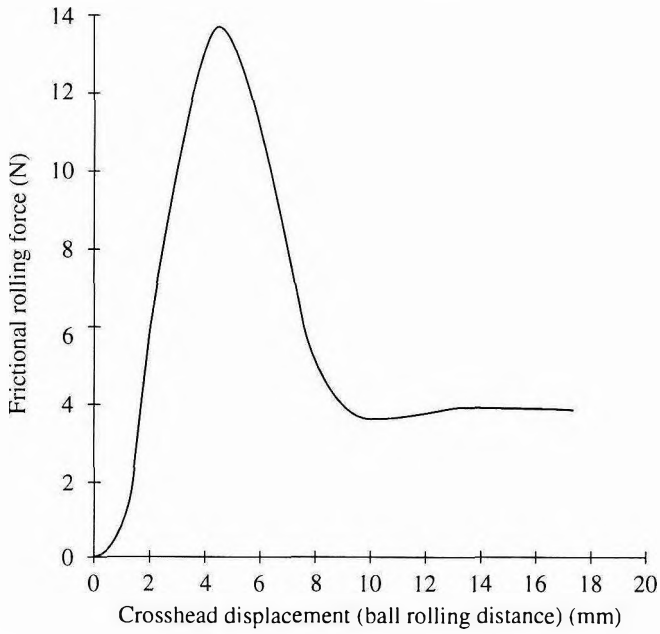


Figure 6. Example of rolling force versus crosshead displacement (NBR Compound No. 4, $t = 2\text{ mm}$, $R = 3.175\text{ mm}$, total load on the four balls = 90 N , dwell time 1000 min).

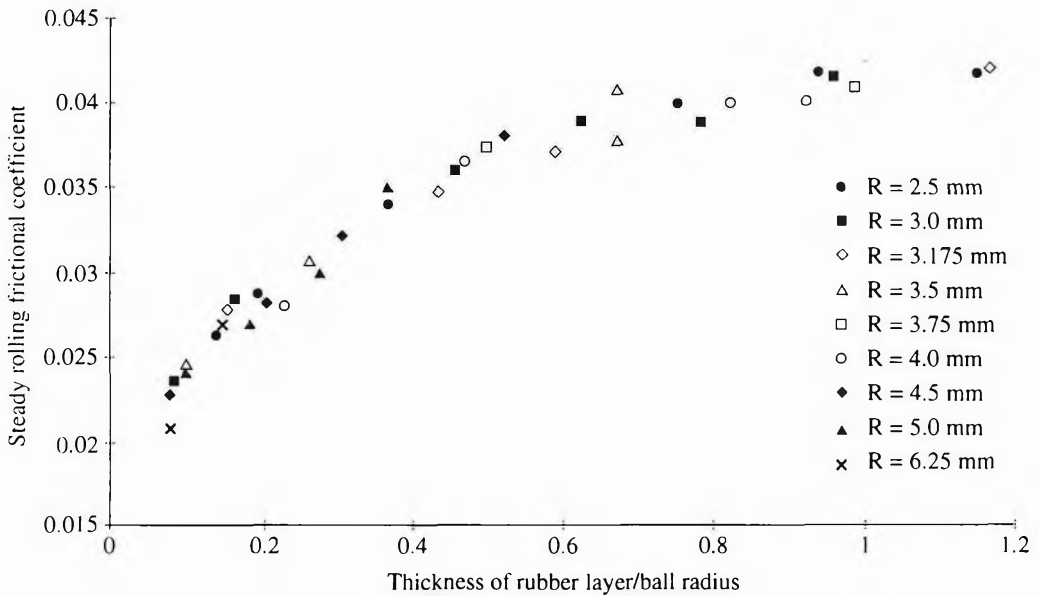


Figure 7. Experimental results for steady rolling friction coefficient on Compound 3 (for W/R^2 held constant at 1.0 MPa) versus ratio of rubber layer thickness t to ball radius R .

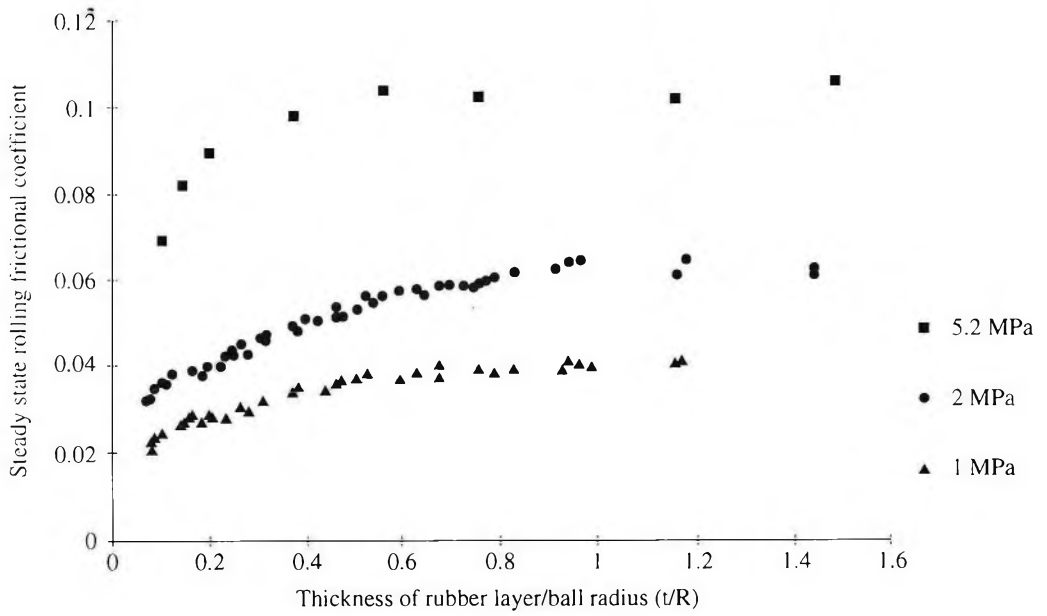


Figure 8. As Figure 7 but including results at different values of W/R^2 (given in MPa as a label for each plot).

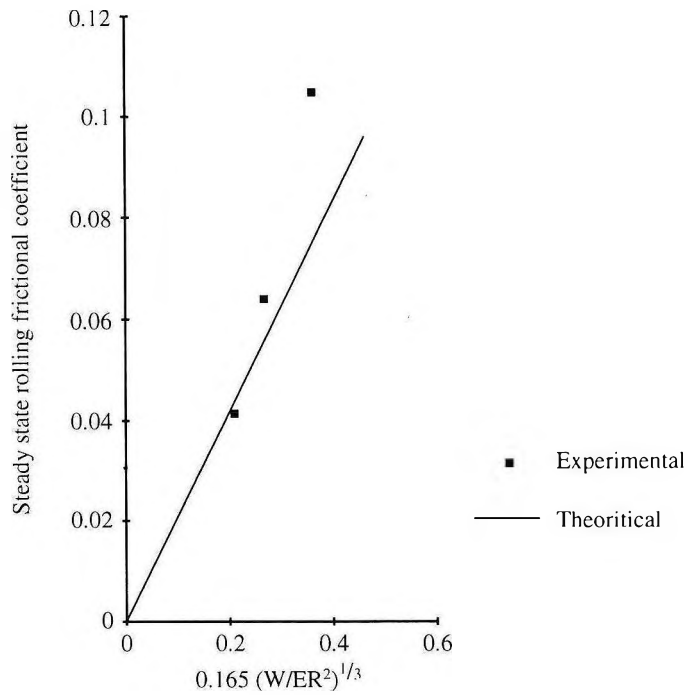


Figure 9. Comparison of theory (Equation 7) with experimental results of steady state rolling resistance as a function of load.

No fracture was observed in the rubber and there was no sign of recovery after 4 months. For the lower stresses ($W/R^2 = 1$ or 2 MPa) the rolling tracks appeared on the rubber surface only temporarily.

Effect of Dwell-time

The peak in the force as the balls roll out from their 'pits' is potentially a problem for the isolation system. If it increases with time it may reach such a high value that the seismic excitation is insufficient to get the system past this peak force, so that it will not operate as intended.

With this in mind a vertical load of 90 N was applied for designated periods of time to sets of four balls ($R = 3.175$ mm, so that $W/R^2 = 2.23$ MPa) between 2.00 mm thick rubber layers. Three different rubbers were used (see *Table 1*). For NBR the surface was used either clean (*i.e.* immediately after peel of the *Mylar* against which it was moulded) or after dusting lightly with talc. The two NR compounds (see *Table 1*) were investigated only after lightly dusting with talc.

The results for peak roll-out force are given in *Figure 10*. It is apparent that the peak roll-out force increases approximately linearly with the logarithm of time. The rate of increase is greatest for the lightly crosslinked NR *Compound No. 3*. For NBR, the effect of talcing the surface is evidently to reduce the rate of increase in peak roll-out force.

It was found that the steady rolling force does not change within experimental error, for the four different rubber samples, over the period of 9 months. *Table 2* gives the average values. The steady rolling force was reduced

TABLE 2. MEAN STEADY ROLLING FRICTION RESULTS FOR PEAK ROLL-OUT FORCE EXPERIMENTS REPORTED IN *FIGURE 10* ($W/R^2 = 2.23$ MPa, $t/R = 0.63$)

Rubber	μ
No. 4 (NBR) clean	0.048
No.4 (NBR) talced	0.040
No. 1 (NR) talced	0.017
No. 3 (NR) talced	0.037

by approximately 13% when the NBR was talced.

The ratio of peak roll-out force to the steady rolling force is highest for the rubbers with higher damping.

The indentation marks or 'pits' on the rubber surfaces are sharply defined after 9 months dwell time, but gradually recovered with time after unloading, being still visible after two months. One way of assessing the recovery is to locate the balls back in the pits at designated times and immediately measure the peak roll-out force. This force falls as recovery proceeds. Such experiments confirmed that recovery is only partial after two months (see *Table 3*). It also shows that the physical formation of 'pits', presumably due to creep, is the main cause of the rise in peak roll-out force with time, at least for talced samples.

DISCUSSION AND CONCLUSIONS

The results confirm that useful magnitudes of rolling resistance can be achieved with the rolling-ball dissipative-layer geometry, using fairly standard rubber compounds. Calculations of the damping ratio of a linear system

TABLE 3. EVALUATION OF PIT RECOVERY AFTER 9 MONTHS DWELL TIME OF NBR (COMPOUND NO. 4) AND NR (COMPOUND NO. 1 AND 3). [NORMAL LOAD PER BALL = 22.5 ± 0.2 N, R = 3.175 MM]

	NBR Compound No. 4 (t = 0.5 mm)	NBR Compound No. 4 (t = 2.0 mm)	NR Compound No. 1 (t = 2.0 mm)	NR Compound No. 3 (t = 2 mm)
1-2 minutes dwell time under constant normal load:				
F_0 = Roll-out frictional force per ball (N)	1.28	1.74	0.76	1.45
9 months dwell time under constant normal load:				
F = Roll-out frictional force per ball (N)	2.42	5.65	2.45	6.35
2 minutes pit recovery from 9 months dwell time:				
$F_{r,1}$ = Roll-out friction force per ball (N)	2.41	5.21	2.38	4.5
% Recovery = $\frac{F - F_{r,1}}{F - F_0}$	1	12	4	38
2 months pit recovery from 9 months dwell time:				
$F_{r,2}$ = Roll-out frictional force per ball (N)	2.29	4.00	1.61	2.58
% Recovery = $\frac{F - F_{r,2}}{F - F_0}$	12	42	50	77

equivalent to *Figure 1* show that it should be relatively easy to achieve values in the typical design range of 0.1 to 0.3, for typical design values of the period *T*.

Although the system behaves well for the largest stresses used ($W/R^2 = 5.2$ MPa), the generation of deep semi-permanent rolling tracks at this stress level suggests it should be

an upper bound for design purposes. As this loading is relatively modest, from the point of view of designing an economical system, it is clear that for all but the lightest structures it is desirable to use a design level for W/R^2 of at least 1 MPa. This stress is still quite large in the context of indentation in rubber; *Figure 9* and a comparison of *Figures 4* and *8* suggest it is beyond the regime of validity of Hertzian

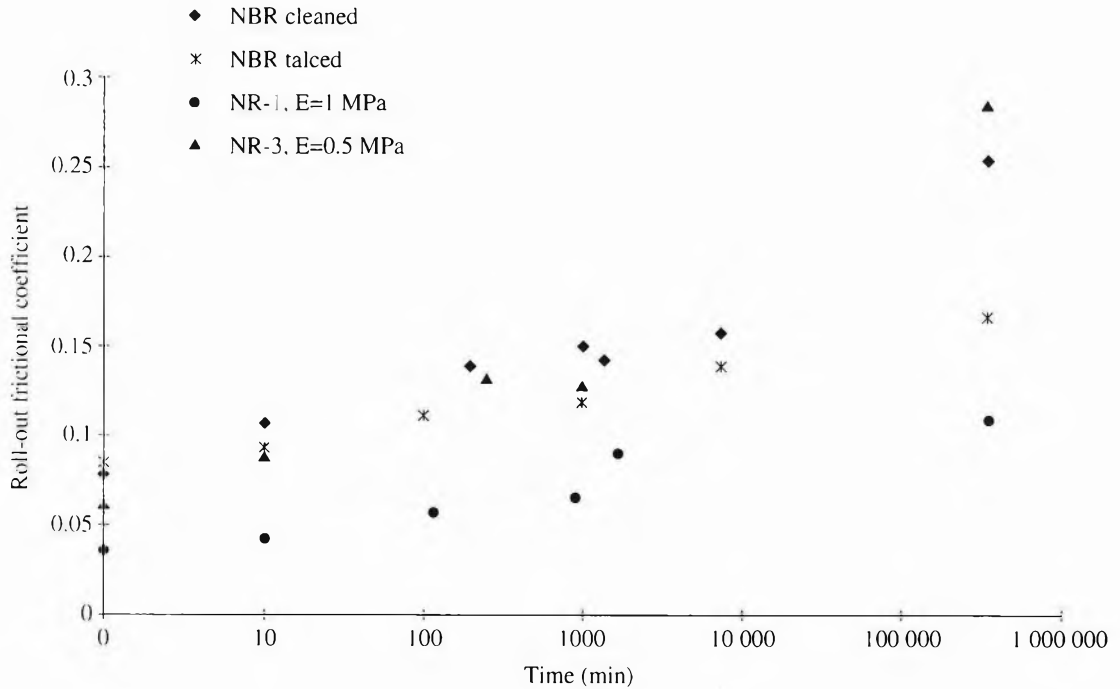


Figure 10. Effect of dwell time on roll-out friction coefficient.

indentation theory or of Waters' empirical modification for layers of finite thickness. In the absence of a method of predicting the rolling resistance theoretically, reliance will have to be placed on prototype test results. However, the experiments are quite straightforward and it is relatively easy to change the rubber compound or its thickness to achieve a target rolling resistance.

The mechanism of generation of the frictional resistance is confirmed to be the hysteresis losses from the moving indentation, as reviewed by Gent and Henry⁴, since there is a strong correlation with the loss tangent of

the rubber while the state of the rubber surface (clean or talced) has a relatively weak effect.

If the balls are held stationary under load for a prolonged dwell-time the peak in force, occurring just before the onset of steady rolling, rises approximately linearly with log time. In the worst case, corresponding to the lightly crosslinked NR *Compound No. 3* after 9 months dwell time, the peak force is 7.6 times the steady rolling value. Such high peak values are a potential problem for the system, since it would not operate correctly unless the seismic excitation is large enough to roll the balls out of their 'pits'. The problem would be serious

if the peak roll-out force exceeds the maximum shear force capability of the isolated structure. One method of mitigating this potential problem is to site the balls on regions of very thin (or more resilient) rubber under static conditions, so that a high roll-out force does not develop. Once rolling, though, the balls could roll onto regions of thicker or more hysteretic rubber to achieve the design level of rolling resistance.

It is concluded that the prolonged isolation system has the necessary versatility to meet typical design requirements. The lighter the structure, the more economic should the system be, since fewer balls will be required. In this way it complements systems based on laminated rubber bearings, since these become relatively more complicated and costly the lighter the structure.

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Influence of Level of Interaction on the Mechanical and Dynamic Mechanical Properties of Thermoplastic Elastomers[†]

ANIL K. BHOWMICK*[#] AND ABHIJIT JHA*

Nylon-6 and acrylate rubber (ACM) were melt-blended in a Brabender Plasticorder at 220°C and 40 r.p.m. rotor speed. The reactive nature of the blend is reflected in the mixing torque behaviour of the blends at different compositions. The solubility characteristics of the blends in formic acid solution gives an approximate idea of the amount of nylon-6 grafted onto ACM and vice-versa. The influence of interaction between the two polymers on the mechanical and the dynamic mechanical properties of the blends are analysed in details and the results are interpreted on the basis of the formation of nylon-ACM graft copolymer at the interfaces. The dynamic mechanical thermal analysis (DMTA) reveals a two-phase morphological structure, indicating incompatibility of the blend components. The grafting reaction results in dramatic increase in both the storage modulus and the Young's modulus of blends. The presence of grafted rubber chains is reflected in the secondary transition of the rubber loss peak at higher temperature. Also, a substantial improvement in the damping properties of the blends in the service temperature range (i.e., 25°C to 175°C) is revealed from the DMTA results. The dynamic vulcanisation of the ACM phase during melt-mixing improves the elongation at break values of the blends.

Reactive blending is known to be one of the most important processes of compatibilisation of two or more immiscible polymers¹⁻³. The two polymers, functionalised with proper reactive groups on their chains react to each other at the interface during mixing at selective temperatures to generate a copolymer which compatibilises the two phases. Coran⁴ reported the properties of thermoplastic elastomers from polyamides/chlorinated polyethylene (CPE) reactive blends. In this paper, we report our observations on the reactive blends of nylon-6 and acrylate rubber (ACM), where the amine

or carboxyl end groups of nylon-6 are expected to react with the reactive epoxy groups of ACM to produce the necessary graft copolymer at the interface during melt-blending operation. The influence of the interfacial reaction on the mechanical and dynamic mechanical properties is highlighted.

EXPERIMENTS

Nylon-6 (*Ultramid B3*) of BASF, GERMANY and acrylate rubber (*NIPOL AR51*) of Nippon Zeon Co. Ltd., Japan and *DIAK#1* of Du Pont

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* Rubber Technology Centre, Indian Institute of Technology, Kharagpur, P.O. Box 721 302, India

[#] Corresponding author

were used for the work. The blends were prepared in batches of 50 gm polymer in a Brabender Plasticoder (PL2000-3) mixer with roller type rotor at a mixer set point temperature of 220°C. The rotor speed was kept at 40 r.p.m. The change of mixing torque with mixing time along with the stock temperature was recorded for each blend. During dynamic vulcanisation, 0.5 p.h.r. DIAK#1 was added to the blends after 8 min of mixing and the mixing was continued for another 5 min after DIAK#1 addition. Test specimens (about 1.2 mm thick) were prepared by compression moulding at 230°C in a frame-and-plate mould between well released aluminium foils for 2 min for all the samples and immediately cooled by passing water under pressure. Solubility of the blend samples was measured in 85% formic acid solution at room temperature and the weight percent of unextracted nylon-6 was calculated. Tensile tests were performed according to *ASTM D412-80* in a Zwick Universal Testing machine (UTM), model 1445. Dynamic mechanical thermal analysis was carried out in a DMTA Rheometric Scientific MK-II model in the blending dual cantilever mode at a frequency of 10 Hz and at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

The reactive nature of nylon-6 and ACM blend is manifested in the mixing torque behaviour of the blends in Brabender Plasticoder at 220°C. Both pure nylon-6 and ACM show a gradual decline in torque (*Figure 1*) with a rise in stock temperature until both reach a steady-state value. But in the case of nylon-6/ACM blends, the mixing torque shows an upward trend after the initial softening (*Figure 1*). This increase in torque can be attributed to the interfacial reaction which may occur between

the two polymers at the processing conditions^{5,6}. During mixing, the melt reaction between the two polymers results in an increase in molecular weight and, therefore, the viscosity of the mix, which raises the torque during mixing. It is also interesting to note that the increment in torque values (*i.e.*, maximum torque minus the minimum torque) when plotted against the weight fraction of ACM (*Figure 2*), passes through a maximum point corresponding to a composition of 55:45 nylon-6/ACM weight ratio. If the increase in torque value suggests the extent of reaction of the polymers, it can be assumed that maximum amount of reaction occurs in the blends with 45 weight percent of ACM. Proportion of ACM on either side of the 45% results in less grafted polymers and hence, lower increment in torque. The solubility data also supports the above observation. The amount of unextracted nylon-6 in formic acid (which is approximately equal to the weight percentage of nylon-6 grafted to ACM chains) of the nylon-6/ACM blends, both dynamically vulcanised and without dynamic vulcanisation, suggests that maximum amount of graft formation occurs near 50/50 (w/w) blend ratio (*Figure 3*).

Figure 4 represents the DMTA results of pure ACM, nylon-6 and 50:50 (w/w) blend of nylon-6/ACM in terms of temperature dependence of $\tan \delta$ in the range between -100°C to 150°C. The blend shows two main damping peaks, one at -2.5°C corresponding to the T_g of ACM (T_g of pure ACM = 0°C) and another broad peak at 85°C due to T_g of nylon-6 (T_g of pure nylon-6 = 98°C). Though peak positions are shifted compared to that of the homopolymers due to interaction between the components, the appearance of two separate $\tan \delta$ peaks suggests the microheterogeneity of the blend (*i.e.*, two-phase morphological structure).

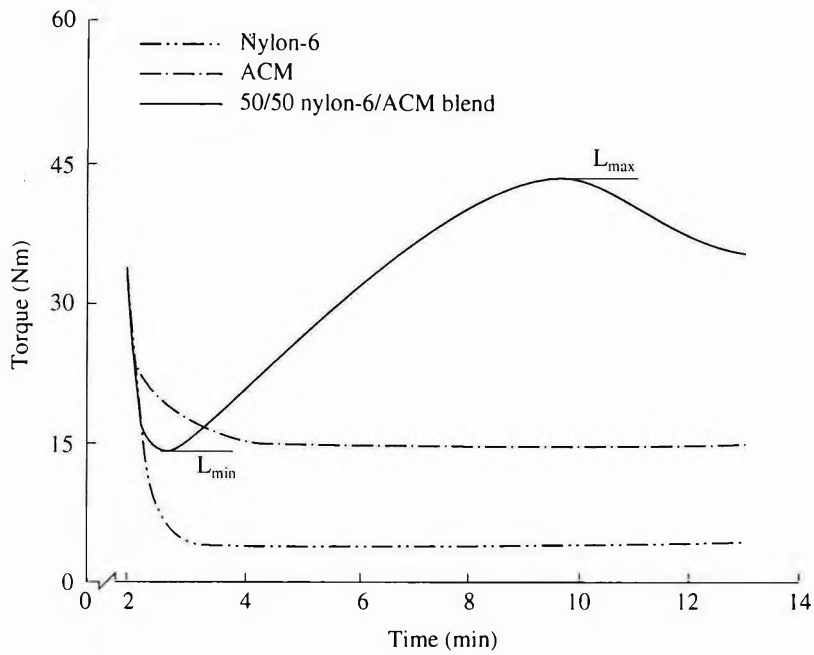


Figure 1. Mixing torque vs. time plot at 220°C and 40 r.p.m. rotor speed.

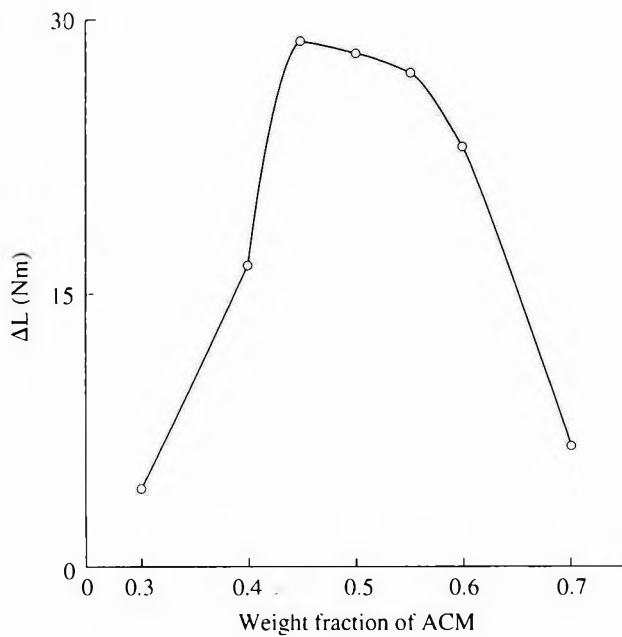


Figure 2 Increment in mixing torque vs. weight fraction of ACM in the blend.

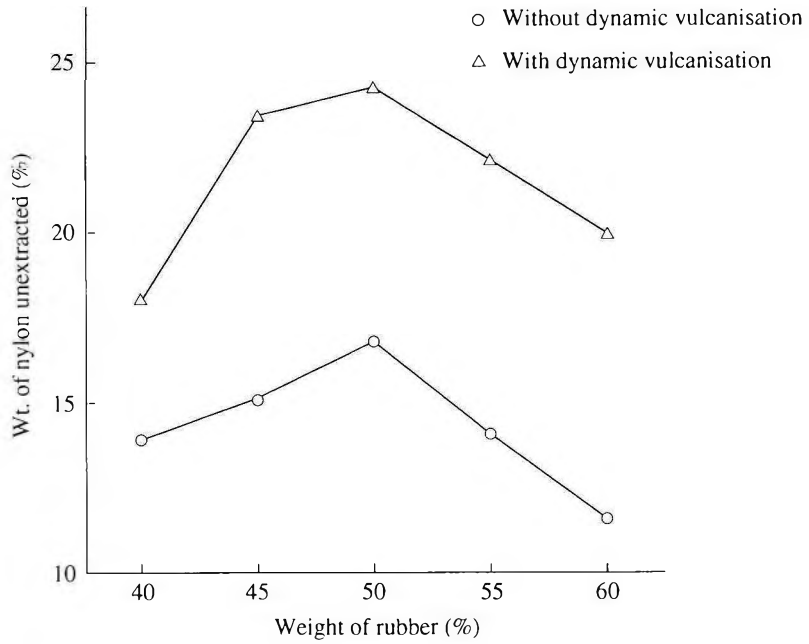


Figure 3. Weight percentage of nylon grafted vs. weight fraction of ACM in the blends.

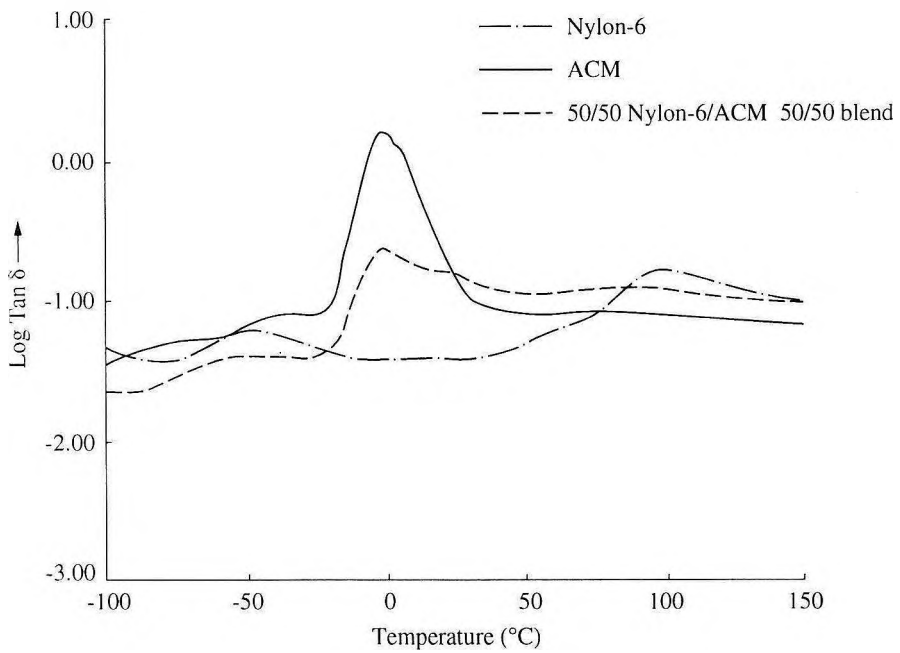


Figure 4. Temperature dependence of loss tangent.

To study the effect of interaction on the dynamic mechanical properties of the blends, the mixing has been carried out to different extents (*i.e.*, for different durations) for 40:60 (w/w) blend and the moulded samples are analysed under identical conditions. *Figure 5* summarises the temperature dependence of $\tan \delta$ and storage moduli, respectively. The $\tan \delta_{\max}$ ($\tan \delta$ at peak position) and the T_g of the ACM phase decrease progressively upto 9 min – 11 min and then increase marginally. T_g of nylon-6 phase displays a progressive decreasing trend with mixing time. The most interesting feature observed in the above case is the appearance of a secondary $\tan \delta$ peak of the rubber phase at high temperature region with increasing level of interaction. In the blends with 9 min and 11 min of reaction, it appears as a shoulder at 13°C and 17°C, respectively, but after 13 min a distinct secondary peak is observed at 22.5°C. This is also reflected in the modulus *vs.* temperature plot (*Figure 5*). As the height of the dynamic transition of a component of a composite apparently reflects the relative quantity of the component itself⁷, the decrease of $\tan \delta_{\max}$ of ACM in the blend is the result of a reduction of the relative quantity of bulk rubber ‘active’ in the dynamic transition. Since the weight fraction of ACM in these blends is constant, the above result can be interpreted by assuming that as the level of grafting increases with mixing time, the relative quantity of bulk rubber is reduced resulting in the reduction of the $\tan \delta_{\max}$ values. The decrease in T_g of ACM phase with interaction can be explained in the light of thermal stress built-up in the outer shell of each of the rubber particles during moulding/cooling due to greater thermal contraction of rubber compared to the glassy matrix. This thermal stress can only be developed when there is

sufficient adhesion between the two phases, generally believed to be secured by the usual grafting operation. As a consequence of this, the free volume of rubber increases and results in a decrease in the glass transition temperature⁸. The decrease in T_g of nylon-6 can also be explained on the basis of the above arguments. It is reported that the segmental motion in chains of a polymer when attached to a more mobile component (*i.e.*, lower T_g) is enhanced in the blend compared to that in the homopolymer. As nylon-6 is grafted to ACM chains which are rubbery in nature, the flexibility of the nylon chains is increased leading to a decrease in its T_g values.

Figure 6 shows the DMTA results of nylon-6/ACM blends with varying amount of rubber content in terms of $\tan \delta$ *vs.* temperature (both dynamically vulcanised and without dynamic vulcanisation). It is clear from the figure, that in case of unvulcanised blends, the $\tan \delta_{\max}$ of the ACM phase increases progressively with increasing amount of rubber content (which is evident from the earlier discussion) and T_g of ACM decreases with increasing plastic content in the blends. As the nylon-6 content in the blends is increased, the radii of the rubber particles are reduced leading to larger interfacial contact area per unit volume of rubber. This results in greater adhesion between the two phases and hence more inclusion of free volume in the rubber phase due to differential thermal stresses developed during cooling. As a result, the T_g of ACM phase decreases with increasing plastic content in the reactive blends. In case of dynamically vulcanised blends, two changes are observed due to crosslinking of the rubber phase: (i) the reduction in the flexibility of the bulk rubber chains leading to higher T_g values compared

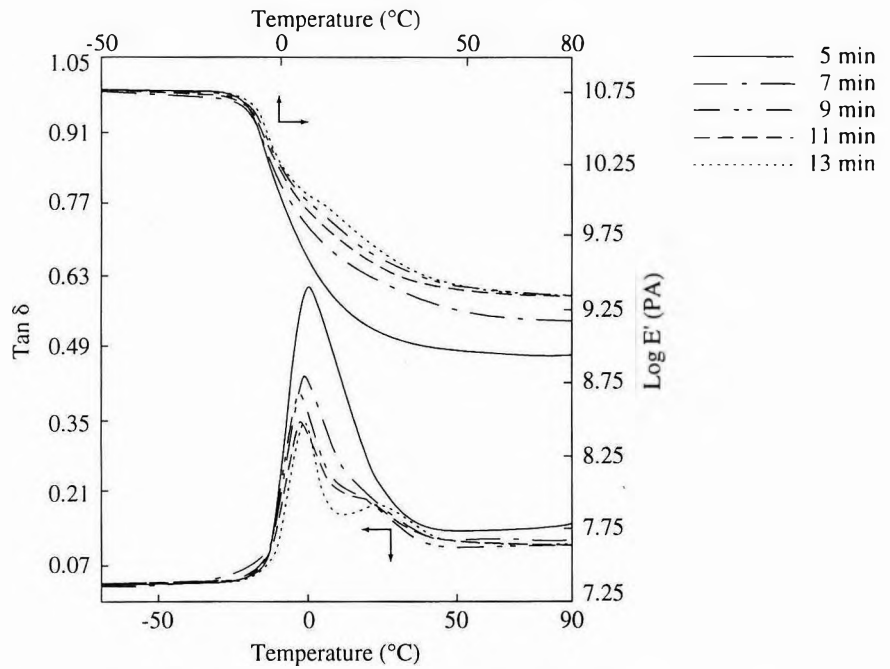


Figure 5. Temperature dependence of $\tan \delta$ and E' of Nylon-6/ACM (40/60) blends interacted for different times.

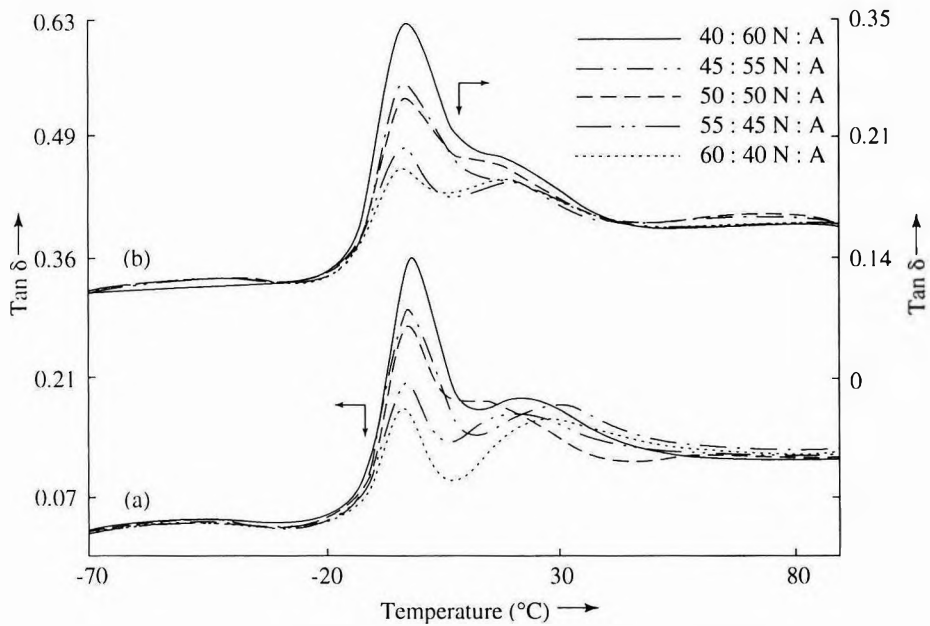


Figure 6. Temperature dependence of $\tan \delta$ of Nylon-6/ACM blends with different plastic to rubber weight ratio, without dynamic vulcanisation (a) and the blends with dynamic vulcanisation (b).

to that of the blends without dynamic vulcanisation, and (ii) the broadening of the loss tangent peak of the rubber phase with a reduction in the height. The effect is more prominent in the blends with higher amount of plastic content.

The mechanical properties of the 40/60 nylon-6/ACM blends are given in *Table 1*. It is observed that both the tensile strength and elongation at break increases as the time of reaction increases. Also, the Young's modulus and the hardness increases progressively to higher values. As the rubber content of this blend is fixed, the increasing trend in mechanical properties is very likely due to interfacial reaction between the two phases, which enhances the adhesion between the two components. It is important to note that both the Young's modulus and the tensile strength of the blend with 13 min of reaction time show an appreciably higher values, resembling that of highly reinforced elastomer systems.

In the case of thermoplastic elastomeric blends with higher amount of plastic content, the tensile strength reaches a value of 19 MPa – 20 MPa and an elongation of about 100% –

120% (*Table 2*). These blends, when dynamically vulcanised, display an increased elongation at break and enhanced tensile strength. However, the Young's moduli and the hardness of the blends are decreased slightly due to vulcanisation.

CONCLUSIONS

Nylon-6 and ACM react to each other in Brabender Plasticorder at 220°C which is manifested in the rise of mixing torque during melt-blending operation. This is also supported by the fact that certain proportions of the nylon-6 in the blends remain insoluble in the formic acid solutions. In the dynamic mechanical analysis, it is observed that both the $\tan \delta_{\max}$ and the T_g of the bulk rubber phase decreased with level of interaction between the two phases which are followed by the appearance of a secondary rubber transition at the higher temperature region (13°C to 22.5°C) for 40/60 nylon-6/ACM (w/w) blend. The interaction increases the Young's modulus and the hardness to an appreciable extent. Also, the tensile strength and the elongation at break increases with the level of reaction. Dynamic

TABLE I. MECHANICAL PROPERTIES OF 40/60 (W/W) NYLON-6/ACM BLEND

Reaction time ^a (min)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Hardness (Shore-D)
5	4	50	20.0	35
7	7	84	23.0	42
9	6	60	29.0	44
11	5	40	29.0	47
13	12	96	37.0	48

^aMixing time at 220°C/40 r.p.m. + 2 min moulding time at 230°C, 10 MPa pressure

TABLE 2. MECHANICAL PROPERTIES OF NYLON-6/ACM BLENDS WITH AND WITHOUT DYNAMIC VULCANISATION^a

Weight percentage of plastic (%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Hardness (Shore-D)
40	12(10) ^b	96(122)	37(30)	48(44)
45	13(13)	90(142)	41(35)	50(47)
50	12(15)	92(140)	45(43)	55(51)
55	19(16)	120(116)	62(56)	57(54)
60	17(20)	100(150)	71(68)	60(57)

^aVulcanised with 0.5 p.h.r. of HMDC

^bThe values in the parenthesis indicate the properties corresponding to the dynamically vulcanised blends.

vulcanisation of the blends results in a slight reduction in hardness, Young's modulus, but the tensile strength and the elongation at break increase.

ACKNOWLEDGEMENT

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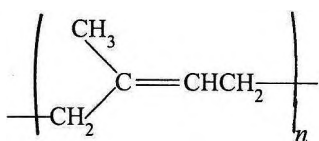
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Use of Mechanistic Principles to Make Modified Natural Rubber Latex Products by Emulsion Polymerisation[†]

NADARAJA SUBRAMANIAM^{*}, ROBERT BALIC^{*}, JOSHUA R. TAYLOR^{*},
MADELEINE GRIFFITHS^{*}, MICHAEL J. MONTEIRO^{*}, ROBERT G. GILBERT^{**},
C.C. HO^{**}, IBRAHIM ABDULLAH^{***} AND PAUL CACIOLI^{****}

A novel class of materials, comprising an artificial polymer inside natural rubber latex particles, so that the new polymer is extensively grafted to the cis-polyisoprene, can be made if the artificial polymer is of very low water solubility, with the natural rubber latex (NRL) used as seed. This avoids the problem of secondary particle formation and subsequent engulfing of the resulting precursor particle into the pre-existing latex particles, which gives inhomogeneities in the conventional means of making modified NRL through such seed technology.

Commercial high-ammonia natural rubber latex (NRL) comprises almost entirely of *cis*-polyisoprene:



stabilised by adsorbed long-chain fatty-acid soap which are hydrolysis products of phospholipids; polypeptides from hydrolysis of the original proteins are also adsorbed on the surface¹. NRL is highly polydisperse in regards to its particle size distribution.

Natural rubber has many advantages for certain applications. An extension of the properties of natural rubber latex would be possible if one could graft a second polymer within a natural rubber latex particle, using the well-established technique of emulsion polymerisation of artificial polymers². Such a novel material could lead to many technical applications, depending for example on the glass transition temperature of the second polymer. Included in the potential advantages of such a process is that natural rubber is a renewable resource.

The reason that one might suppose that extensive grafting of a second polymer would

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^{*} School of Chemistry, University of Sydney, NSW 2006, Australia

^{**} Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

^{***} Faculty of Pure and Applied Science, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

^{****} Ansell International, P.O. Box 144, 75912 Melaka, Malaysia

Corresponding author

be possible is as follows. Normally, second-stage growth would result in separation of the two phases, because of the incompatibility of any two different polymers (above a minimal molecular weight). However, given reasonable reactivity ratios, one might expect that sufficient grafting of the second polymer into the double bond on the *cis*-polyisoprene; this would result in the formation of *in situ* compatibiliser which should prevent the separation of the *cis*-polyisoprene and the new polymer. However, as is well known, if one attempts to perform such a growth using conventional seeded technology, the resulting product is highly heterogeneous (see, for example Reference 3); effectively, a 'fruit-cake' morphology results. This heterogeneity is evidenced both by the morphology as seen in electron microscopy studies and also in T_g data, where it is seen that the glass transition temperature of the product of such a polymerisation has a peak corresponding exactly to that of natural rubber.

We postulate here that an origin for the heterogeneity observed when NRL is used as a seed is that *secondary particle formation* occurs easily (for reasons discussed in the next section); the new particles so formed tend to be subsequently engulfed by the soft NRL particles (*Figure 1*). These domains are then rich in the second polymer, and so become the principal locus for subsequent polymerisation, resulting in heterogeneity.

MECHANISMS OF PARTICLE FORMATION AND RADICAL ENTRY

The mechanisms for particle formation and of entry of radicals into pre-existing particles in an emulsion polymerisation are well established². These mechanisms are illustrated in *Figure 2*, for a system where the concentration of surfactant is below the cmc,

with persulphate initiator. The most important parts of the mechanism for the present purposes comprise the *competition between entry and particle formation*: an aqueous-phase radical formed from initiator can grow to a critical degree of polymerisation z , when it becomes surface-active and may enter a pre-existing particle⁴, or may grow further until it reaches another critical degree of polymerisation j_{crit} , when it collapses to form a new particle by homogeneous nucleation⁵.

It is thus apparent that avoidance of secondary particle formation involves this fundamental criterion of the competition between entry and particle formation⁶. There are several means of doing this (*e.g.*, controlling the initiator type or number density of pre-existing, or seed, particles), since to some extent one may control each of the various mechanisms in *Figure 2* separately.

Over the years, techniques have been developed² for obtaining unambiguous values for entry rate coefficients in emulsion polymerisation systems. The optimal method for this involves using growth in a seeded system, in the absence of secondary particle formation, and choosing conditions so that particle growth is controlled by 'zero-one' kinetics; entry of a radical into a particle which already contains a growing radical results in instantaneous termination, so that particle growth involves only propagation, entry and exit (desorption). The kinetics of radical loss are then obtained by initiating with γ radiolysis and then removing from the γ source, which yields the exit rate coefficient. The steady-state rate with a chemical initiator is then measured, from which a knowledge of the exit rate coefficient then yields that for which radicals from the chemical initiator enter the particles.

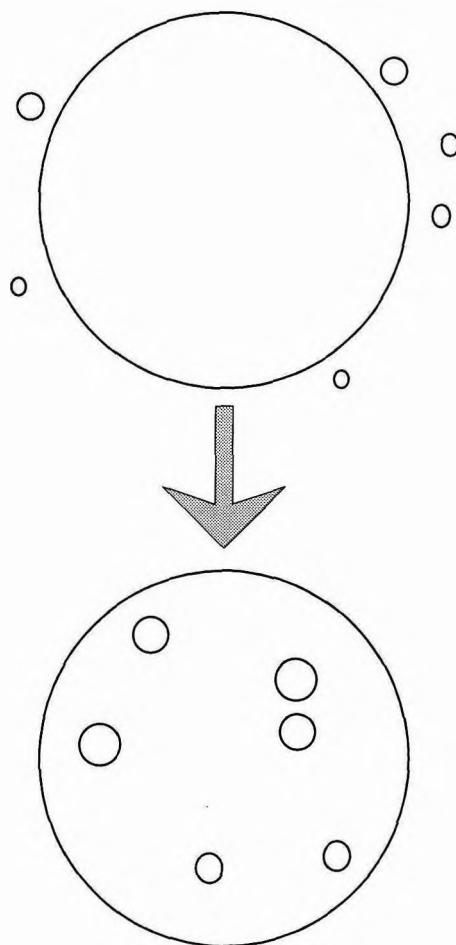


Figure 1. How secondary nucleation followed by engulfment can lead to a "fruit-cake" morphology.

What is especially important for controlling secondary particle formation in NRL is that such studies have shown that the presence of any polymeric layer around the particles has a dramatic effect on the kinetics: *inter alia*, the rate coefficient for entry is greatly reduced⁷. It has been postulated that this reduction is because the 'hairy layer' of polymer surrounding the particle slows down the rate at

which a z-mer diffuses through the interfacial regime. For systems stabilised by *anionic* surfactant, there is considerable evidence^{4,7,8} that the diffusion of a z-mer through the interfacial layer which is one of the mechanisms for particle entry shown in *Figure 2* is not rate-determining, whereas this step probably is rate-determining for systems containing *polymeric* stabiliser (αr , in the case of NRL,

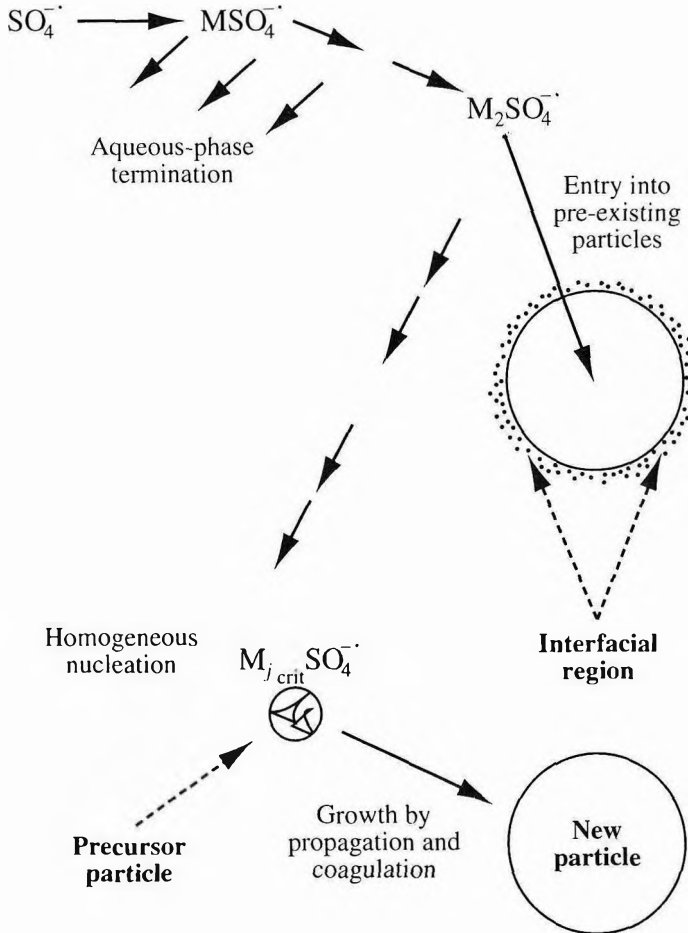


Figure 2. Particle formation and growth in an emulsion polymerisation below the cmc.

where there is adsorbed hydrolysed protein around the particles).

This reduction in the entry rate coefficient for a system such as NRL, together with our postulate that inhomogeneity derives at least in part from particles formed by secondary nucleation being subsequently engulfed within

NRL particles, explains why it seems so difficult to have extensive grafting in a NRL: the reduction in the entry rate coefficient implies that radicals which otherwise would have entered tend instead to form new particles, which are subsequently engulfed and form domains.

STRATEGY FOR AVOIDING SECONDARY PARTICLE FORMATION IN NRL

The forgoing postulate suggests that extensive grafting in NRL requires avoiding secondary particle formation. One way might be to try an initiator such as AIBN, which being hydrophobic will form radicals within the particles. However, this initiator is sufficiently soluble in the aqueous phase that some radicals can form in the aqueous phase as well as within the particles, and so this will not avoid secondary nucleation. Instead, a suitable strategy to avoid secondary particle formation and thus bring about extensive grafting⁹ would be to use a system where formation of j_{crit} -mers is impossible. This can be effected by carrying out the polymerisation with a monomer that is *highly insoluble in water*, as well as choosing a initiator which produces hydrophobic radicals. Use of a highly hydrophobic monomer for the modification of NRL means that radicals can only be formed in the NRL particles; moreover, because the monomer is highly hydrophobic, exit of radicals formed by transfer is minimal,¹⁰⁻¹² and aqueous-phase propagation of any exited radical to a sufficient degree of polymerisation to form a precursor particle is unlikely. All in all, secondary particle formation should be obviated.

One suitable hydrophobic monomers for this purpose is vinyl *neo*-decanoate (Veo Va-10[®] or Neo-10[®]). We have measured the solubility of this monomer in pure water as about 4×10^{-5} mol dm⁻³.

A procedure to implement this strategy is as follows⁹. The ammoniated NRL is swollen with the monomer (note that this requires some time,

since the low water solubility means slow transport across the aqueous phase). A suitable initiator is chosen, one example of which is cumene hydroperoxide (CHP) and tetraethylene-pentamine); the hydrophobic nature of the CHP ensures newly-generated radicals will be unlikely to be present in the water phase. A suitable surfactant is chosen such that coagulation of the NRL does not coagulate; appropriate surfactants can be chosen from the type used for synthetic rubber¹³. Polymerisation can be effected in a number of ways, including batch and semi-continuous (where the redox initiator is injected either in shots or continuously).

RESULTS

In order to test for the absence of secondary nucleation, the procedure described above was performed on differentiated NRL, where smaller particles are removed by centrifugation: in the particular case here, the NRL sample used contained no particles smaller than 300 nm. The presence of new particles can then be detected by examining particle size distributions by both transmission electron microscopy and by capillary hydrodynamic fractionation (CHDF).

When an NRL was used as a seed for second stage growth with *styrene*, the particle size distributions showed extensive secondary particle formation. However, when the same procedure was followed with vinyl *neo*-decanoate, no particles smaller than the original NRL were observed, as expected from the preceding mechanism-based discussion.

The next test for the expected occurrence of extensive grafting is from an examination of the T_g . Particular care must be taken in the

technique used for this purpose. For this, we employ MTDSC (modulated thermal differential scanning calorimetry), where the modulated heating helps reduce artifacts due to kinetic rather than thermodynamic properties of the polymer. *Figure 3* compares the thermograms so obtained for four different samples: (a) NRL without any artificial polymer, and three samples prepared by polymerising an artificial polymer as above, using (b) methyl methacrylate, and (c) vinyl *neo*-decanoate. The unmodified NRL and MMA-modified samples both show essentially the same T_g : -65.4°C and -65.3°C (the MMA sample also exhibits a much higher T_g corresponding to MMA, although that is not shown in the figure). This is as expected, since the MMA is sufficiently water-soluble that secondary nucleation is expected to occur readily. The T_g with the NRL samples wherein vinyl *neo*-decanoate was polymerised is however quite different: -60.9°C (the mass of new polymer was about 10% of that in the NRL); again, a higher T_g was also seen in each case, corresponding to the second polymer. Moreover, the MTDSC trace does not return to the baseline between the two T_g maxima.

This increase in the T_g of the rubber polymer for this water-insoluble monomer is consistent with significant grafting having taken place, either as a (semi-)IPN or at least involving microphases of the two polymers.

RATE DATA

Rate data, obtained by dilatometry calibrated by gravimetry, show some unexpected behaviour. While MMA systems polymerise at similar rates to those seen in ordinary seeded emulsion polymerisations, vinyl *neo*-decanoate polymerises much more slowly, as shown in

Figure 4. This is despite the very high propagation rate coefficient of vinyl *neo*-decanoate, as measured by pulsed laser polymerisation¹⁴.

This slow rate is not due to some peculiarity of the kinetics of seed emulsion polymerisation of vinyl *neo*-decanoate, since the rate of seeded polymerisation of this monomer in a butyl acrylate seed (which is of course also rubbery, like NRL) is quite fast. Possible reasons for the slow rate of this monomer in NRL compared to the fast rate of the other species may be one or all of the following reasons:

- (a) The radical species formed by initiator and vinyl *neo*-decanoate may be particularly reactive towards protein, and/or
- (b) This radical species may form a relatively stable species with the backbone double bond in natural rubber (*i.e.* unfavourable reactivity ratios), and/or
- (c) The grafting with vinyl *neo*-decanoate is so effective that the particles cannot swell fully when polymerisation has gone beyond a certain conversion, and so form a polyisoprene-rich core and a vinyl *neo*-decanoate monomer-rich shell, with very high rates of termination in the latter.

Of these, (b) is unlikely, since the initial rate in *Figure 4* is seen to be quite fast; this observation also suggests that (a) is unlikely. The high effectiveness of grafting which is suggested by the remaining explanation, (c) is consistent with the larger change in the T_g for vinyl *neo*-decanoate.

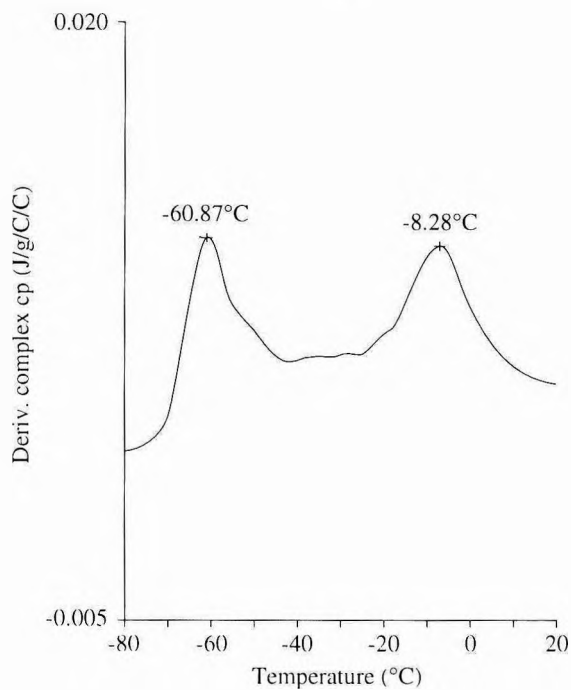
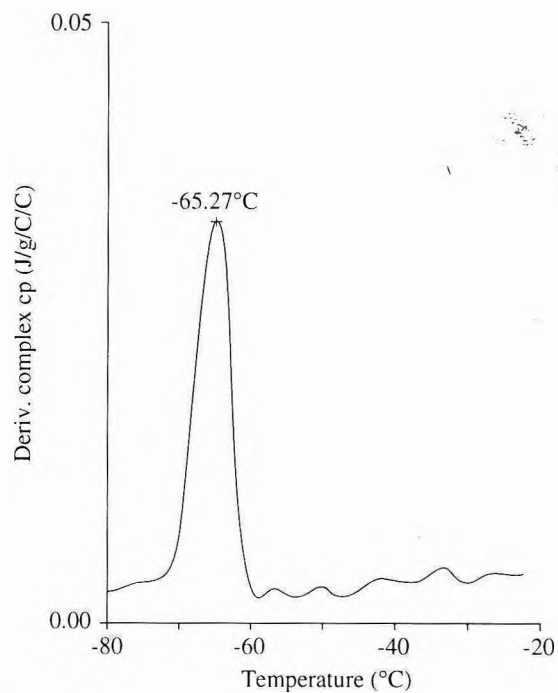
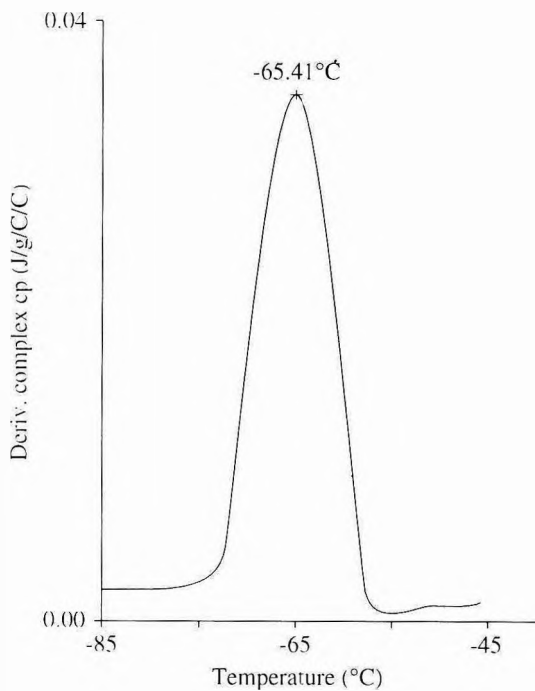


Figure 3. MTDSC thermograms of natural rubber, of NRL modified by seeded polymerisation with MMA, and of NRL modified by seeded polymerisation with vinyl neo-decanoate.

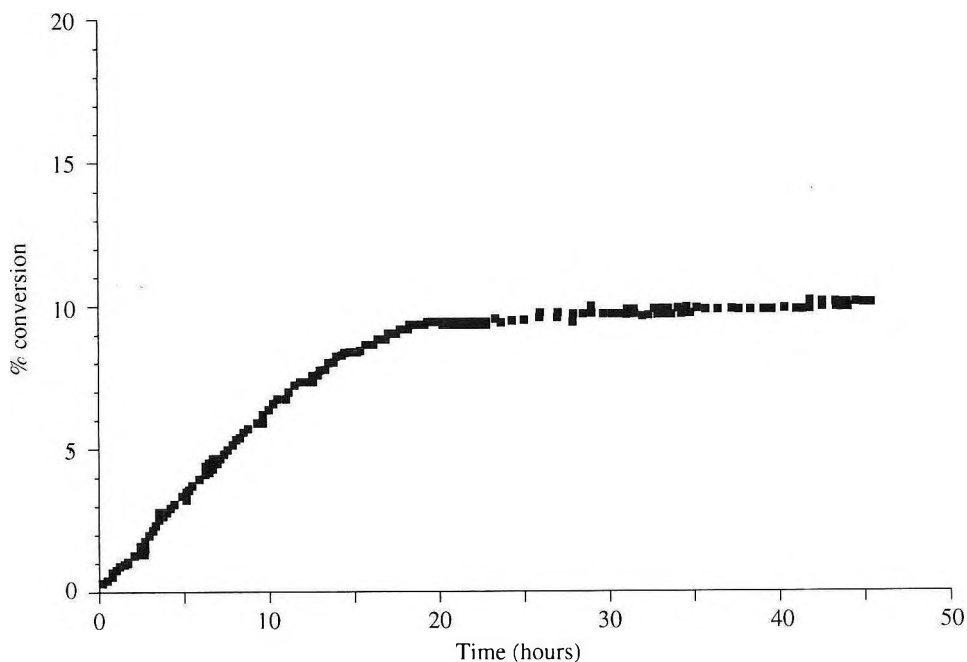


Figure 4. Conversion as a function of time for a 1:1 natural rubber + vinyl neo-decanoate system, initiator $3 \times 10^{-4} \text{ mol dm}^{-3}$ persulphate plus 2% mercaptan at 50°C .

CONCLUSIONS

The production of a modified ammoniated natural rubber latex by performing polymerisation with these latices as seed for growth with a highly hydrophobic monomer leads to a product where the T_g data are consistent with the formation of a relatively homogeneous (semi-)IPN or grafted micro-phases, as expected from mechanistic arguments based on the avoidance of secondary particle formation. There are some mechanistic questions which require further work, especially

the reason for the slow rate of polymerisation seen with vinyl *neo*-decanoate.

ACKNOWLEDGEMENTS

The support of the Australian Department of Education, Employment, Training and Youth Affairs for a Targetted Institutional Links Grants is gratefully acknowledged, as are the support of Union Carbide (for RB) and of the Australian Research Council. We also appreciate the collaboration of the University of Sydney Electron Microscope Unit and of Olga Schaffer of Lehigh University.

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Proteins Eluted from Natural Rubber Crumb[†]

ROY G.O. KEKWICK*

The protein eluted from vulcanised natural and styrene butadiene rubber crumb samples has been subjected to total amino acid analysis and the total protein estimated. An antiserum raised to the NR crumb eluate reacted with the homologous immunogen and with polypeptides of the C-serum of fresh Hevea latex. The allergenicity of the natural crumb eluate has been compared to that of hevein in skin prick testing.

The possible sources of sensitisation to rubber latex proteins are unclear. One possibility is that the population may be frequently exposed to low doses of latex proteins as a result of inhalation of respirable particles of vulcanised rubber possibly present in urban air, originating from rubber tyre wear. The presence of such particles in particulate air samples derived from a rotary impaction air sampler stationed 7.4 m above ground level and 48 m from a moderately travelled road, has been demonstrated by Brock Williams *et al.*¹. An extract obtained from rubber tyre millings, the protein concentration of which was not specified, was found to inhibit the interaction of 6 out of 7 specimens of sera from latex sensitive persons reacting with a commercial preparation of latex allergens to a similar extent to that obtained with a latex glove protein extract containing 1 mg protein per ml. A further communication from the same group² claims the 'tentative' identification of a 50 kD polypeptide reacting with latex specific IgE in immunoblots of abraded tyre extracts.

In contrast to the above findings the *in vivo* tests of Yip *et al.*³ failed to demonstrate allergenicity of vulcanised rubber extracts in

skin prick testing of a panel of 31 latex sensitive patients. Whilst all of the patients responded to the different glove extracts tested none of the subjects responded to extracts obtained from samples of vulcanised rubber. There was however no indication of the protein levels in the extracts used save that those of the extracts of vulcanised rubber were apparently less than 4 µg/ml. Yip *et al.*³ also carried out RAST inhibition assays using a similar commercial latex allergen preparation to Brock Williams *et al.*¹, and with a calibrated pool of serum containing anti-latex IgE were unable to detect appreciable levels of allergen in any extract. Again the protein concentration in none of the tested samples was given.

More recently Miguel *et al.*⁴ have compared the extractable protein from latex gloves with that of dust from truck and radial car tyres. A pool of sera from latex allergic subjects was found to bind to specific peptides in immunoblots of electrophoretic separations of both truck and car tyre extracts.

With this conflict of evidence in mind it appeared desirable to establish the presence or

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* School of Biochemistry, University of Birmingham, Birmingham, B15 2TT, UK

otherwise of proteins associated with fragments of vulcanised rubber prior to any possible environmental survey of the presence of such respirable fragments in the atmosphere. To this end the eluates obtained from vulcanised rubber crumb have been analysed and tested for immunogenicity and antigenicity.

MATERIALS AND METHODS

Rubber crumb, vulcanised SBR and NR rubber was kindly provided by Dr A.D. Roberts of the Tun Abdul Razak Laboratory. Extracts were prepared by shaking the crumb (100 g) with phosphate buffered saline containing 0.01% merthiolate and 0.01% NaN_3 (400 ml) for 16 h at room temperature. The extract was filtered and concentrated to about 5 ml by pressure dialysis, centrifuged and freeze-dried. The freeze-dried material was reconstituted in 1.0 ml water and applied to a 10 ml *Sephadex G-25* column from which it was eluted with distilled water. The eluate was monitored by absorption at 280 nM and by assay using the Bradford protein assay⁵. Electrophoresis in polyacrylamide gels containing sodium dodecyl sulphate SDS PAGE was carried out according to the procedure of Laemmli⁶. Immunoblots were obtained by the method of Towbin⁷. Total amino acid analyses were made on material hydrolysed in HCl for 24 h at 110°C. Antisera were obtained after 4 successive immunisations of each approximately 25 µg in Freund's adjuvant at fortnightly intervals.

RESULTS

Elution of the concentrated extracts from both NR and SBR rubber from *Sephadex G-25* columns showed the presence of high and low molecular weight components absorbing at 280 nM and both components gave a wavelength absorbance shift to 595 nM when

tested with Coomassie blue in the Bradford assay (*Figure 1*).

Analysis by SDS PAGE of extracts of both NR rubber showed the presence of a polydisperse range of polypeptides, the principle components having molecular weights of 58, 54, 43, 34 and 32 kDa. Amino acid analysis of the hydrolysate of the high molecular weight component of the extracts gave the results shown in *Figure 2*. From these results it was calculated that the eluted protein from the NR rubber crumb comprised approximately 0.23 p.p.m. vulcanisate and that of the SBR rubber 0.045 p.p.m. vulcanisate.

Immunisation of a rabbit with the NR extract gave an antiserum reacting with NR crumb polypeptides with approximate molecular weights of 100, 32, 29, 20 and 18 kDa and with those of C-serum with molecular weights of 100 (strongly) and 25 and 21 (weakly). The antiserum did not react with the proteins of the bottom (lutoid) fraction of latex.

Skin prick testing of 6 selected latex allergic persons showed that whilst 5 gave a positive response to hevein (a major latex allergen), only one responded to the NR crumb extract (each at a concentration of 10 µg/ml).

DISCUSSION

It appears from the above results that whilst vulcanised crumb has associated protein, the level of elutable protein is approximately three orders of magnitude less than that usually found associated with latex goods, the SBR sample studied had a level of associated protein about one fifth of that of the NR crumb. These protein values obtained from total amino acid analysis were a thousandfold less than those reported by Miguel *et al.*⁴ using indirect methods of analysis.

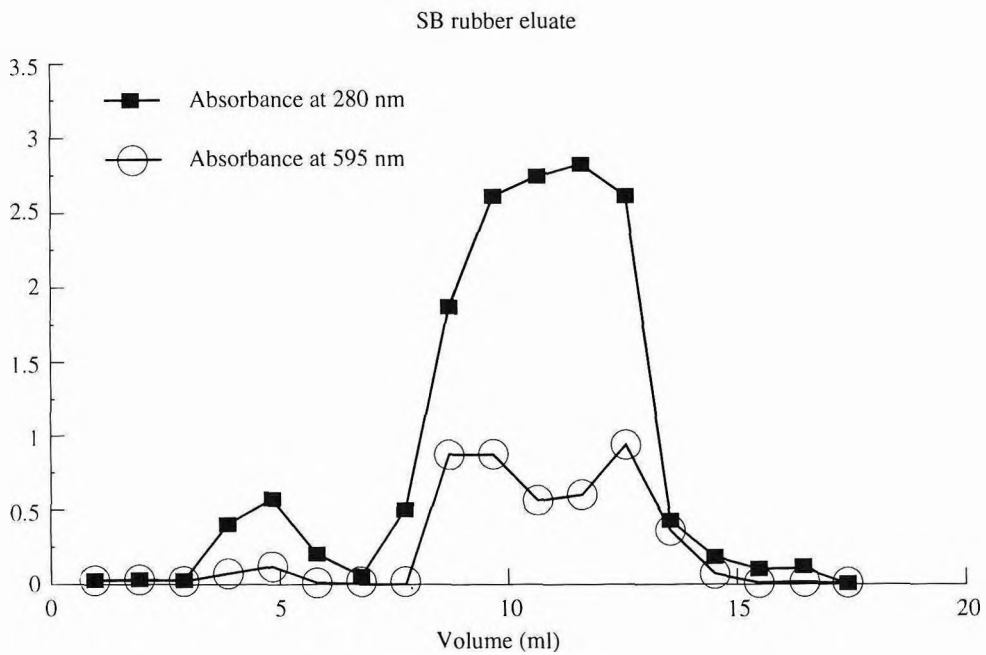
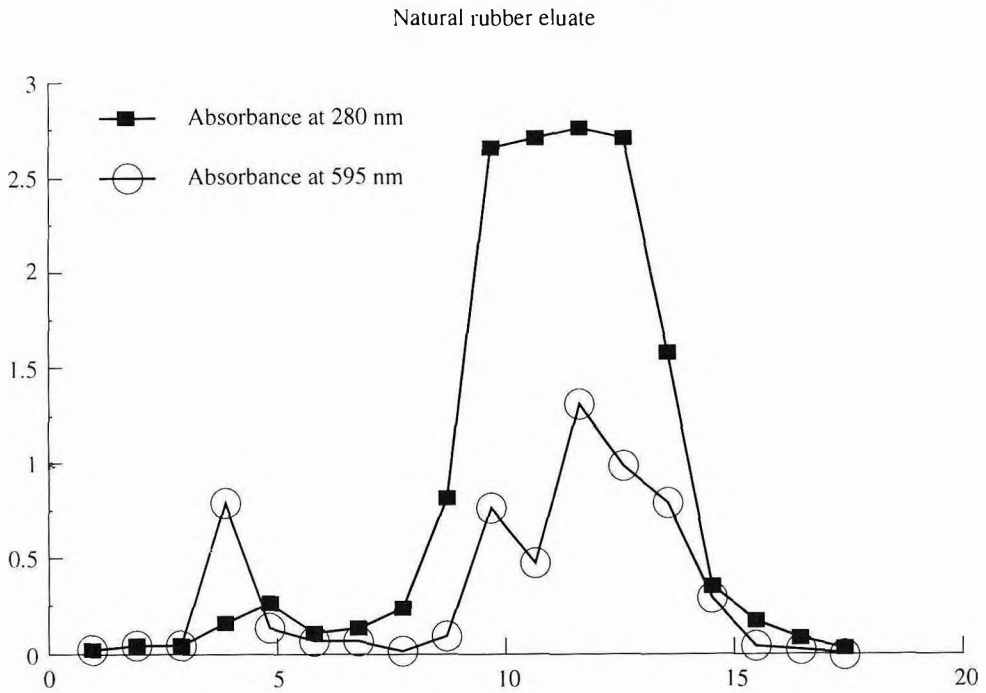


Figure 1. Elution of rubber eluates from Sephadex G-25. Absorbance at 595 nm indicates monitoring by the Bradford assay.

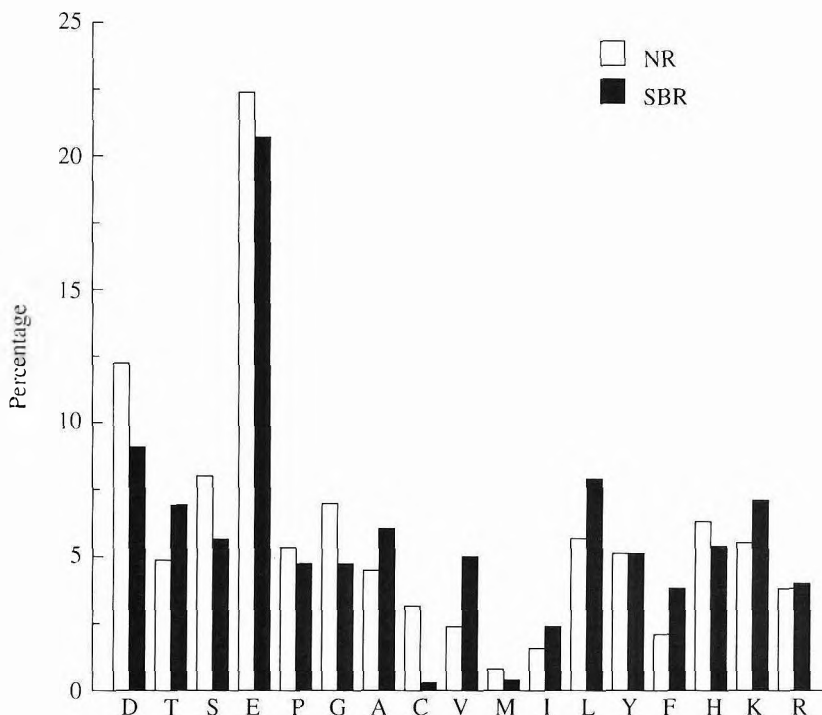


Figure 2. Amino acid analysis of rubber eluates.
The single letter code for amino acids is used.

It is therefore concluded that whilst vulcanised NR crumb does have a trace of associated antigenic protein, it is far lower than that reported for tyre dust measured by indirect methods. Thus if the protein in vulcanised NR crumb approximates to that of tyre dust, the potential sensitisation risk should be considerably less than would appear from the studies of Brock Williams *et al.*¹ and Miguel *et al.*⁴. This is borne out to some extent by the sample of patients subjected to skin prick testing.

ACKNOWLEDGEMENT

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Functionally Graded Polyurethane Elastomers Prepared by Electrophoresis of Monomer[†]

MUTSUHISA FURUKAWA^{*#}, TAKAHIKO OKAZAKI^{**} AND TETSURO SHIIBA^{*}

A novel preparation method of functionally graded interpenetrating network polymer (IPN)-type elastomers, was proposed. Functionally graded IPN-type polyurethane elastomers (PUEs) were prepared by electrophoresis of ionic monomers. The base PUEs were prepared from poly(oxytetramethylene)glycol (PTMG) and/or poly(oxyethylene)glycol (PEG), 4,4'-diphenylmethane diisocyanate (MDI), and a mixture of 1,4-butane diol with trimethylol propane (TMP). Ionic monomers used were methacrylic acid and quarternary N,N-dimethylamino ethyl acrylate. Effects of the electrophoresis time of monomer on morphologies and mechanical properties were studied by DSC, polarising microscopy, etc. Spherulite sizes of the modified PUEs depended significantly on the electrophoresis time. Abrasion resistance of the surface of IPN-type PUEs evaluated by DIN abrasion test was better than that of non-treated PUE.

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with general purpose elastomers. These characteristics are utilised in a wide variety of industrial products, which are industrial parts, building materials, sports goods, daily necessities, and medical equipments. These properties are strongly dependent on chemical structures and superstructures of PUEs¹⁻⁵.

In recent years, investigation of graded multicomponent polymers has been conducted. Okinaka *et al.*^{6,7} studied binary polymer mixtures, poly (2-chlorostyrene)/poly (vinyl methyl ether), undergoing phase separation

induced by a temperature gradient. Kano *et al.*⁸ designed gradient polymer materials made by acrylate adhesive/fluoro-copolymer blends and analysed gradient structure by depth profiling using PAS-FTIR and TEM observation. Composition exponentially varied in the vicinity of surface, while that of the internal region was nearly constant. In the previous paper⁹, we proposed a new preparation method of functionally graded PUEs by temperature gradient casting. These PUEs have gradient morphology with spherulite graded size. Thermal and mechanical properties, and abrasion resistance of these were also graded.

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^{*} Department of Materials Science and Engineering, Faculty of Engineering, Nagasaki University,

^{**} 1-14 Bunkyo-machi, Nagasaki 852, Japan

Central Research Laboratory, Bando Chemical Industries Ltd., 3-1-6 Ashihara-dori, Hyogo-ku, Kobe 652, Japan

[#] Corresponding author

In this study, we proposed a novel preparation method of the functionally graded interpenetrating network polymer (IPN)-type elastomers. The functionally graded IPN-type polyurethane elastomers were prepared by electrophoresis of ionic monomers; methacrylic acid and quaternary N,N' -dimethyl ethyl acrylate. Effects of the electrophoresis time of monomer on morphologies and mechanical properties were studied by DSC, polarising microscopy, *etc.*

EXPERIMENTAL

Preparation of PUEs

PUEs were prepared from poly (oxytetramethylene) glycol (PTMG: Mn = 2000, Sanyo Chemical Industries; Japan) and/or poly (oxyethylene) glycol (PEG : Mn = 2000, Sanyo Chemical Industries), 4,4'-diphenyl methane diisocyanate (MDI: Nippon Polyurethane Industries, Japan), and a mixture of 1,4-butane diol and trimethylol propane (75/25 wt%) as a chain extender by a prepolymer method. Prepolymers were prepared from PTMG or PTMG/PEG (50/50 wt%) and MDI [(NCO)/(OH)] = 3.30 at 70°C for about 3 h under nitrogen atmosphere. The prepolymer and chain extender [(NCO)/(OH)] = 1.05) were well-mixed for 90 s and the viscous reaction product was poured into a mould heated at 130°C. The viscous product was cured for 1.5 h at 130°C. After this period, a sheet of 2 mm thickness was demoulded, then the sheet was post-cured at 110°C for 24 h under air atmosphere.

Preparation of Functionally Graded IPN-type PUEs

Synthetic scheme of PUEs is shown in *Figure 1*. PUEs were swelled in a mixture of

solvent with radical initiator and a curing agent at ambient temperature for 24 h. These swelled PUEs were put in an apparatus for electrophoresis as shown in *Figure 2*. Ionic monomer was added into one of the cells and was moved by impressing voltage during required time. The vinyl monomer included in PUEs was polymerised at 70°C.

Slicing of PUE Sheets

PUEs of 2 mm thickness was sliced up to five pieces (about 0.4 mm thickness) by a splitting machine (Fortuna Werke Maschinen fabrik AG, Model NAF-470-D, Germany). These sheets obtained are used for the following testings.

Measurement of Density

Density was determined by weighing of sample in air and water.

Measurement of Gel Fraction

Gel fraction was measured by weighing method after equilibrium swelling in benzene or N,N -dimethyl acetamide (DMA) at 60°C.

Thermal Analysis

Thermograms were recorded with the aid of DSC (Rigaku Electric Inc. Japan; Thermo Plus, DSC-8230) at heating rate of 10°C/min from -150°C to 250°C under nitrogen atmosphere.

Observation of Micro-domain Structures

Micro-domain structures were observed by using a polarising microscope (Nikon, OPTIPHOT2-POL, Japan) equipped with a heating stage (LINKAM, TH-600PM). A

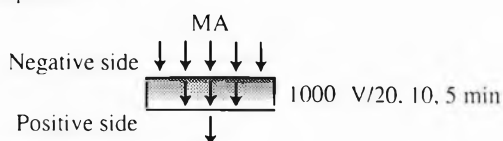
1. Equilibrium swelling of PUE with electrophoresis solution



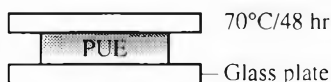
2. Set to the electrophoresis apparatus.
and addition of MA to the side of negative electrode

Reference to Fig. 2

3. Electrophoresis



4. Polymerisation of MA



5. Drying

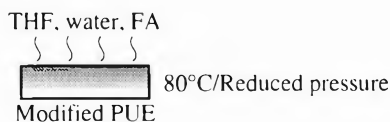


Figure 1. Preparation scheme of functionally graded PUEs by electrophoresis (Example; MA as monomer).

sensitive colour plate (530 mm) was used for birefringence analysis.

RESULTS AND DISCUSSION

Functionally Graded IPN-type PUEs with Polymethacrylic Acid

PMA IPN-type PTMG-PUEs. Methacrylic acid (MA) of 3 wt% to solvent was added into the cell equipped with cathode. A mixed solvent

of THF and water (75/25 vol%) was used. When voltage of 1 kV was impressed between both electrodes, initial current value of system was 1 mA. This value was held at 5 min and 10 min of electrophoresis time. However, current value increased to 2 mA at 20 min of electrophoresis time. This result shows that MA monomer ion ($\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO}^-$) passed through the PUE sheet from the cathode side to the anode side. PTMG-PUE as control was white translucent, while PMA IPN-

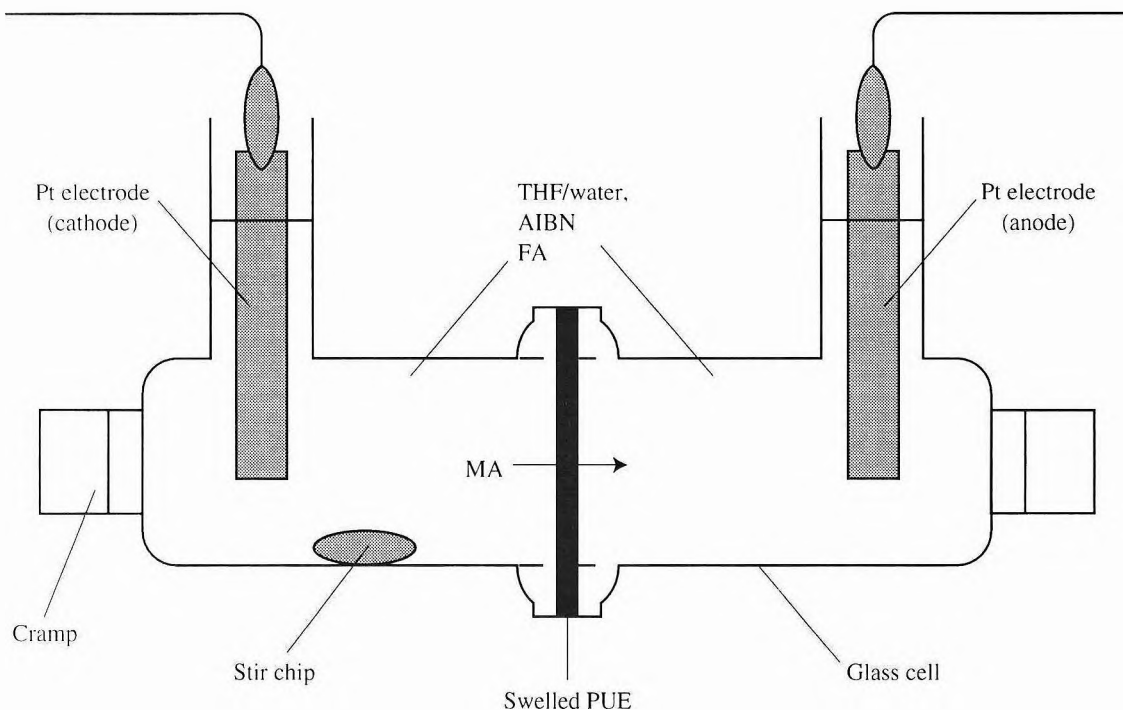


Figure 2. Apparatus for electrophoresis.

type PTMG-PUE which was prepared by electrophoresis at 5 min and polymerisation of MA, was light yellowish translucent. The appearance of this IPN-type PUEs changed from light yellowish translucent to deep yellowish translucent with increasing electrophoresis time.

Figure 3 shows polarising micrographs taken at the surfaces of both electrode sides in each PMA IPN-type PTMG-PUEs. Figure 3 shows

also those of the surfaces of PTMG-PUE in which MA was diffused naturally from the negative electrode side to that of the positive electrode side for 20 min. The PTMG-PUE as control had 'negative spherulites' with well-defined Maltese cross, which had a diameter of 25 μm – 35 μm . However, the structure of the spherulites of the IPN-type PTMG-PUE prepared at electrophoresis time of 5 min turned into small spherulites. Though the matrix part in the surface of the positive electrode side

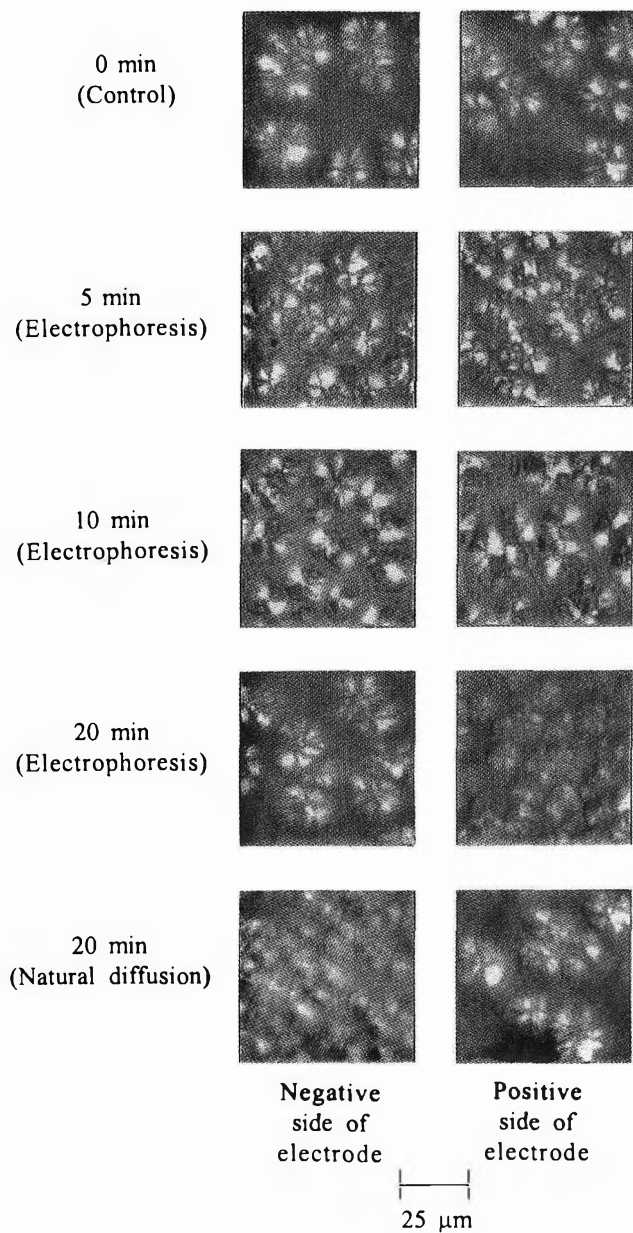


Figure 3. Polarising micrographs of each surface in PMA IPN-PTMG-PUEs prepared by electrophoresis.

was of smooth surface and that of the negative electrode side was slightly of uneven roughness. In the IPN-type PTMG-PUE prepared at 10 min, the spherulites observed in both surfaces looked like that of those at 5 min, however, the matrix part of the surface in the negative side of electrode had lost the unevenness and the surface in the positive side of electrode became rough, that is, the surface state of sample obtained at 10 min were reversed. While the dimension of spherulites on the surface of the negative side of electrode in the IPN-type PTMG-PUE at 20 min was the same as that in control PUE, and that on the surface of the positive side of electrode was smaller than that in control PUE and spherulites were broken and the surface was rough.

As MA was naturally diffused from one side to the other side of PUE sheet for 20 min, the surface contacted with MA was as rough as the surface on the positive side of electrode at 20 min and appearance of another surface did not change. These results indicate that the rate of diffusion of MA is significantly faster and that concentration of PMA in each layer is controlled easier in the electrophoresis method than in the natural diffusion method.

Abrasion resistance evaluated by DIN abrasion tester for each surface at electrophoresis time of 5 min and 20 min are shown in *Figure 4*. The specimen obtained by electrophoresis revealed better abrasion resistance than control. In the comparison of surfaces between the negative and positive side of electrodes, the surface of the negative side of electrode obtained at electrophoresis time of 5 min and that of the positive side of electrode at 20 min had better abrasion resistances. These results indicate that PMA-rich phase in PMA IPN-type PTMG-PUEs have

excellent abrasion resistance because formation of PMA IPN PUEs increase the apparent crosslinked density.

PMA IPN-type PTMG/PEA-PUEs. PTMG/PEG (weight ratio = 1/1)-PUEs were used as base PUEs in place of PTMG-PUEs in order to increase swelling ratio of PUEs in water and decrease the time of electrophoresis.

Figure 5 shows polarising micrographs taken at sliced samples of PMA IPN-type PTMG/PEG-PUEs prepared at 1 min and 4 min of electrophoresis. *Figure 5* shows also the surfaces in which MA was diffused naturally from cathode side to anode side for 3 min. In the PMA IPN-type PTMG/PEG-PUE prepared at electrophoresis of 1 min, the size of the spherulites was increased to the order of negative side of electrode < middle < positive side of electrode. While the globular pattern was observed in the matrix part at the negative side of electrode, these patterns were not observed at middle part and positive side of electrode. With increase of electrophoresis time (4 min), the size of the spherulites was increased to the order of the positive side of electrode < middle < negative side of electrode. The globular pattern was observed in the matrix part at each specimen. In the IPN-type PTMG/PEG PUE prepared by natural diffusion at 3 min, the size of the spherulites was decreased in the negative side of electrode only.

Figure 6 shows DSC thermograms of each part of the sliced specimen of these PUEs with PMA and PTMG/PEG PUE. T_g of PTMG/PEG-PUE was observed at about -70°C and -30°C , assigned to micro-Brownian motion of PTMG and PEG residues, respectively. Recrystallisation and melting of soft segment domain were also observed at about -10°C and

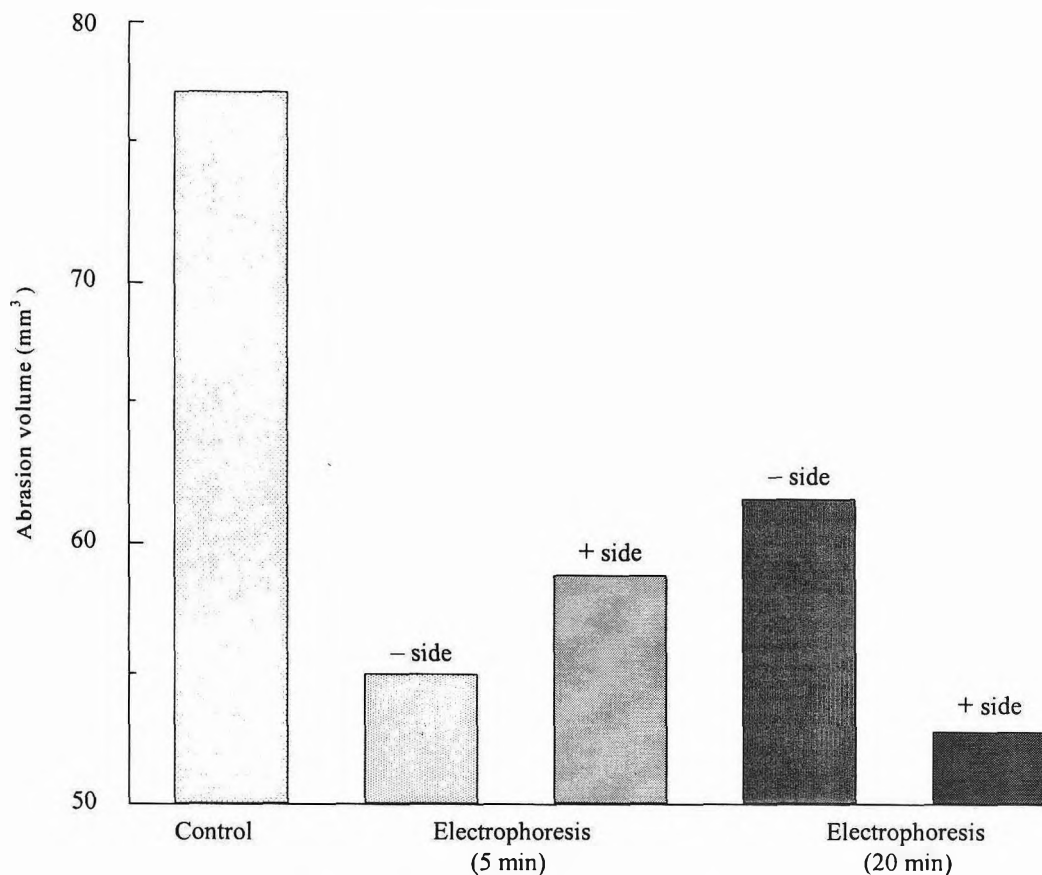


Figure 4. Abrasion volume evaluated by DIN abrasion tests for PMA IPN-type PTMG-PUEs prepared by electrophoresis.

15°C. In the IPN-type PTMG/PEG-PUEs prepared at 1 min or 4 min of electrophoresis, T_g was slightly differed for each parts. However, behaviour of recrystallisation and melting of soft segment domains significantly differed for each part. In the IPN-type PUE prepared at 1 min of electrophoresis, specimen of the negative side of electrode did not show the recrystallisation behaviour. The middle part specimen had a small peak of recrystallisation. That of the positive side of electrode had

significant recrystallisation and the melting behaviour was same as that of control. When MA diffused by 4 min of electrophoresis, the specimen of the positive side of electrode did not show the recrystallisation behaviour. That of the negative side of electrode had significant recrystallisation and melting behaviour same as that of control. On the other hand, each specimen of the PUE prepared by natural diffusion method did not indicate recrystallisation behaviour. These results show

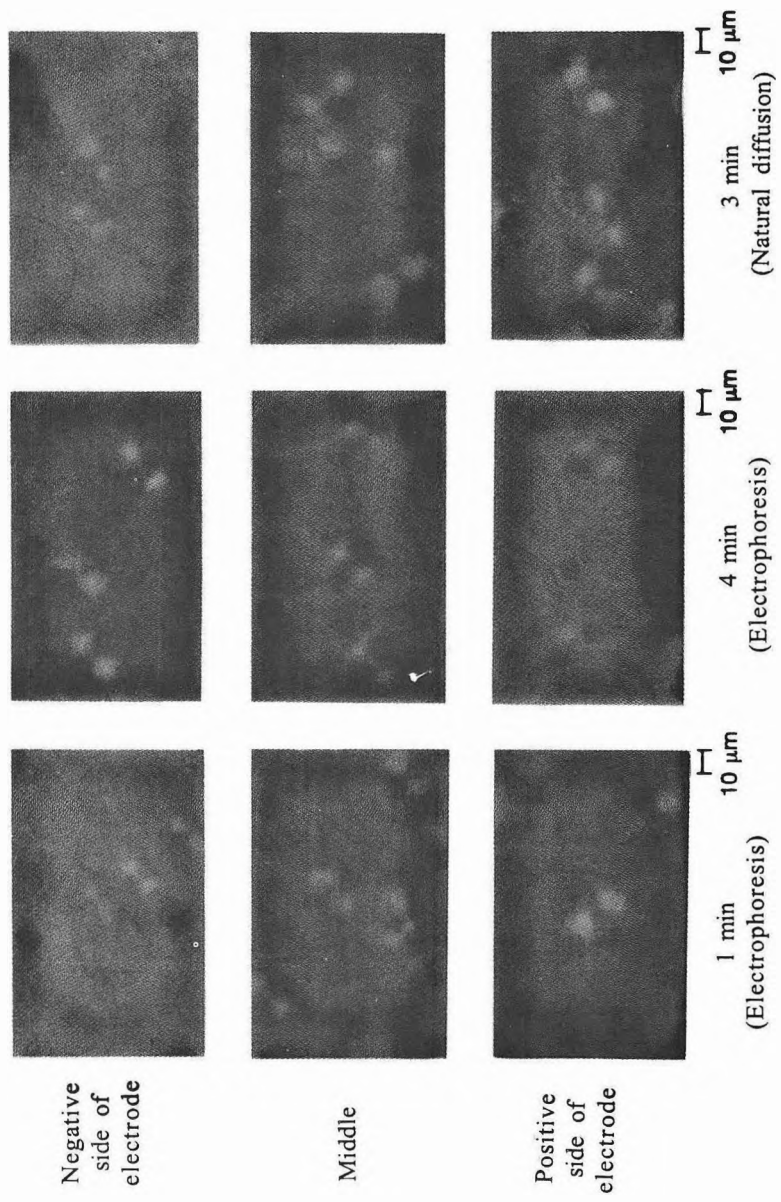


Figure 5. Polarising micrographs of each surface in PMA IPN-type PTMG/PEG-PUEs prepared by electrophoresis.

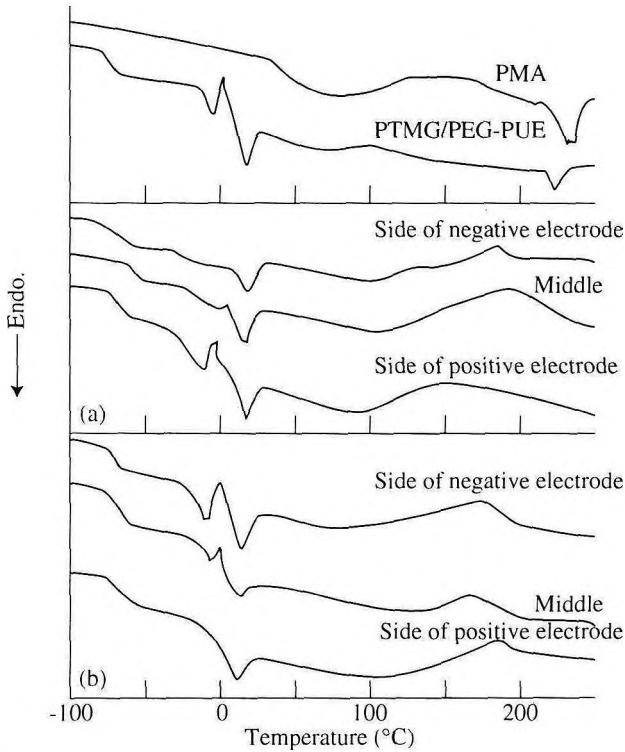


Figure 6. DSC thermograms of PMA IPN-type PTMG/PEG-PUEs prepared by electrophoresis. Time of electrophoresis is 1 min (a) and 4 min (b).

the following: 1) PEG induced to base polyurethane increased the rate of diffusion of MA; 2) PMA in these PUEs has a concentration slope.

Functionally Graded IPN-type PUEs with poly(quaternary N,N'-dimethyl aminoethyl acrylate)

Quaternary dimethylaminoethyl acrylate (DMAEA) is used as a cationic monomer. This monomer was supplied as 80 wt% aqueous

solution. In this case, methanol was used as solvent DMAEA, *N,N'*-methylene-bis-acrylamide as a curing agent and PTMG/PEG PUEs as base PUEs. DMAEA (3 wt% to solvent) was diffused from positive side of electrode by electrophoresis (350 V, 1 mA, and 10 min).

In polarising micrographs at each specimen in PDMAEA IPN-type PTMG/PEA-PUE, the sample of positive side of electrode had small 'negative spherulites' with well-defined Maltese

cross and globular part in matrix phase. However, the structures of the spherulites specimen on the middle and negative side of electrode had the same or a little smaller dimension as that of control. These results also indicate that these spherulites of positive side are due to the degradation of aggregation of hard segments by interpenetrating PDMAEA. Nitrogen content determined by elemental analysis was 2.89% for control, 9.78% for PDMAEA, 3.00% for positive side, and 2.95% for negative side. From these results, content of PDMAEA for positive side was 1.6 wt%, while that for negative side was 0.87%, under this condition.

CONCLUSION

In this study, we proposed a novel preparation method that functionally graded IPN type PUEs be prepared by electrophoresis of ionic monomer into the base polymers and polymerisation of monomer. Size and structure of spherulites of the modified PUE have been graded. The thermal properties of the modified PUE were also graded. This method has the advantage of the slope where concentration is controlled easily. Further regulation of voltage and time of electrophoresis is possible in the synthesis of novel high performance polymers

which can be utilised in industrial parts, building materials and chemomechanical devices.

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Truck Tyre Developments and their Effect on Natural Rubber Consumption[†]

M.E. CAIN* AND PHILIP J. WATSON*#

In 1995 some 240 million truck tyres (radial, bias and cross-ply) were produced, of which about 38%, or 90 million tyres, were those referred to as heavy commercial vehicle (HCV), with remainder being light commercial vehicle (LCV) tyres. The elastomer content of HCV tyres is about 70%–90% natural rubber and for LCV tyres is about 65% natural rubber. The paper analyses these statistics and elastomer contents in relation to the importance of truck tyres as major end-uses of natural rubber. The factors influencing the future use of natural rubber in truck tyres are examined, and some predictions of future demand are made. The possible influence of this major end-use on the natural rubber price is considered.

Truck (or commercial vehicle — CV) tyres are defined by the European Tyre and Rim Technical Organization (ETRTO) as those having a size 8.25–16 and above, where 8.25 represents the tread width of the tyre in inches and 16 is the rim diameter in inches. The term ‘commercial’ covers a vast range of vehicles from light trucks to heavy lorries, and the tyres fitted to these then are normally referred to as light commercial vehicle (LCV) or heavy commercial vehicle (HCV) tyres, with HCV tyres defined as those having a cross-sectional tread width of 10 inches or greater. These larger tyres are normally used for long-distance haulage work on large rigid trucks, tractor units and trailers or road-trains, or on passenger coaches and buses. In industrialised countries, CV tyres are virtually 100% radial construction with a life-span of about two or three times that of similar cross-ply tyres.

TYRE FUNCTIONS

Tyres are the vital component between a vehicle and the road surface. They support the weight of the vehicle and transmit steering, accelerating, decelerating and braking forces. Moving tyres are in a constant state of deformation — blending, expanding and flexing — in response to forces received from the road surface. To perform these functions satisfactorily, truck tyres must:

- Be strong enough to withstand the inflation pressure required by the imposed weight of the laden vehicle;
- Provide an effective combination of traction, steering control and skid resistance and give acceptable mileage in the service in which they are used; and

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* International Rubber Study Group, 8th Floor, York House, Empire Way, Wembley HA9 0PA, UK

Corresponding author

- Withstand the stresses and strains caused by road shocks and heat build-up, particularly during long journeys, often at high speed.

Ever since the production of the first pneumatic tyres in the 1880s it has been the aim of tyre makers to fulfil these functions. However, improvements in one area have usually only been achieved at the expense of other areas. The search has been for an optimum balance of properties, a particularly onerous objective bearing in mind the changing needs of customers, raw material developments and the demands of economic necessity. Therefore, it is not surprising that tyres have developed by a series of 'trade-offs'.

USAGE OF TRUCK TYRES

Truck tyres have also developed within the specialisation of LCV and HCV for particular service requirements by fleet operators. This has resulted in HCV (radial-ply) tyres being designed for three specific wheel configurations or tyre-vehicle systems:

- Steering axle — with a ribbed tread pattern designed for uniform wear across the tread face, water dispersion and handling characteristics;
- Driving axle — with a lugged tread pattern for traction and better wear; and
- Trailer — with a ribbed tread pattern for cool running temperatures, improved tread wear and fuel economy.

The majority of trucks, especially in the industrialised countries, are managed by fleet operators who are particularly interested in the fuel economy of their operation. The primary

contributory factor to fuel economy in fleet operations is the skill of the driver, but other important factors are:

- Vehicle design — type of vehicle, aerodynamic aids, side-gap seals, engine specification and drive train;
- Vehicle operations — speed, type of freight and gross vehicle weight;
- Environment — temperature, topography, weather and road surface; and
- Tyres — wheel alignment, axle configuration, inflation pressure, tyre construction and type.

For fleet operators, fuel is one of their primary variable costs and this expense is expected to increase in the future. Truck tyres have a significant impact on a vehicle's fuel consumption, as it has been estimated that they account for about one-third of the energy dissipation of a loaded tractor-trailer combination. The rubber compounds used in the manufacture of the tyre play a critical role in its rolling resistance characteristics, especially in the tread and shoulder areas.

Although the overriding factor controlling the development of LCV and, more especially, HCV tyres is economy; truck manufacturers also stress the importance of safety in their performance characteristics. Operators of both truck and bus fleets are very conscious of both tyre and fuel costs, much more so than the average motorist. Consequently, truck tyre wear, including irregular wear, is a major concern for fleet operators. Tyre tread wear—*i.e.* the abrasion of the tyre tread—is a cyclical process. Between each contact with the road surface the tread segment remains essentially

at rest. During contact with the road, abrasion and stressing occur, with part of the energy dissipated in the form of heat. Recovery of the tread then takes place so that energy can again be dissipated at the next contact with the road surface. This process of tyre tread wear, which determines the useful life and durability of a tyre, depends on a multiplicity of factors, including cornering frequency and speed, acceleration/braking levels, vehicle drive configuration, tyre inflation pressures, load factors, wheel alignment, road systems and surfaces, and topography/climate.

The main causes of uneven or irregular wear — poor alignment and incorrect tyre pressures — can be controlled by fleet operators with proper maintenance procedures. The two major factors influencing the fleet operator's decision to purchase tyres are performance and economy. Multi-retreadable and regroovable radial truck tyres provide truck and bus fleet operators with the options of using new or retreaded tyres to reduce their costs per operating mile. There are basically six main categories of fleet operators and their general preference for truck tyres is detailed below:

- International and long distance hauliers — mainly new HCV tyres;
- Medium size fleet hauliers (middle distance) — new and retreaded HCV tyres;
- Small fleet operators (middle distance) — new and retreaded HCV tyres and new LCV tyres for vehicles for local deliveries;
- Local delivery fleet — new and retreaded LCV tyres (as well as car tyres for car-derived vans);

- Tipper and on/off road operations — mainly retreaded HCV tyres for tipper uses, and new and retreaded HCV tyres for on/off road applications;
- Large fleet bus/coach operators — mainly new HCV tyres for long distance and retreaded HCV tyres for local operations.

The commercial vehicle industry has been affected in recent years not only by their own 'cost-consciousness' but also by the environmental issue of fuel economy of both light and heavy trucks as a means of conserving energy. This is particularly important for large fleet operators since it has been estimated that an improvement of 10% in tyre rolling resistance in truck tyres can improve fuel consumption by 2%– 4%. Tyre construction is a major factor in determining rolling resistance, and the change from cross-ply to radial construction has reduced this by up to 30%. Recent developments in the truck tyre industry have not only been concerned with the longevity of the life of the tyres, but also with improvements in compounding to give lower rolling resistance.

TRUCK TYRE STATISTICS

The development and growth of world production of truck tyres by major producing countries from 1975–95 is shown in *Figure 1*. The production of CV tyres is affected by the number of commercial vehicles produced annually (original equipment demand, *Figure 2*) and the demand for replacement tyres for the CVs in use (truck parc, *Figure 3*). The production of commercial vehicles has grown steadily with occasional downturns, whereas the commercial vehicle parc has advanced uniformly upwards over the period.

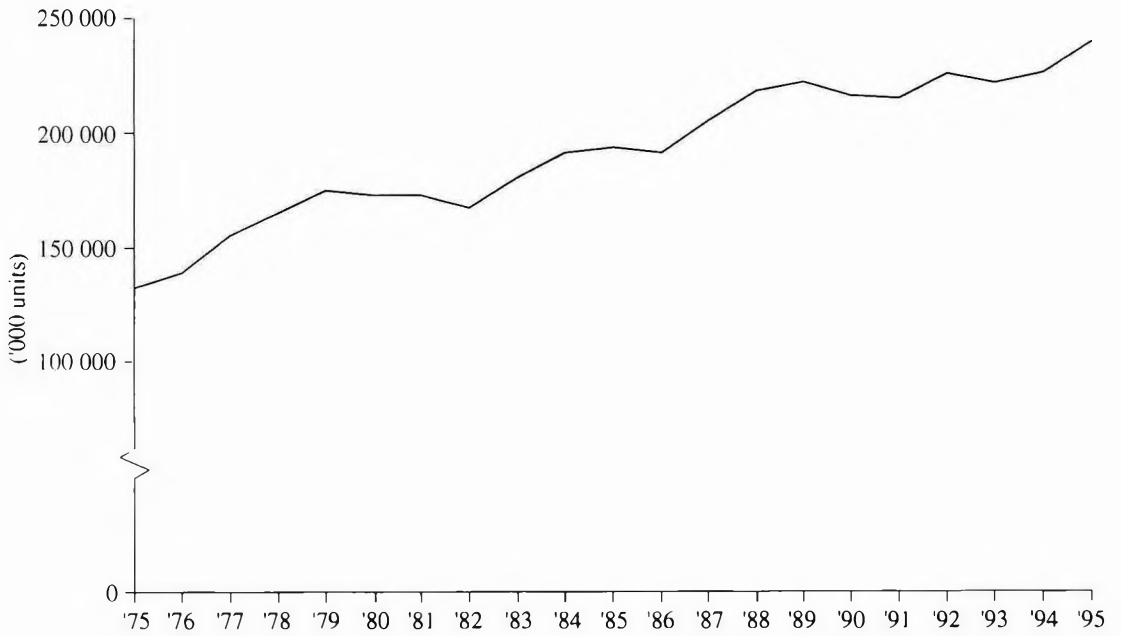


Figure 1. World CV tyre production 1975 - 1995.

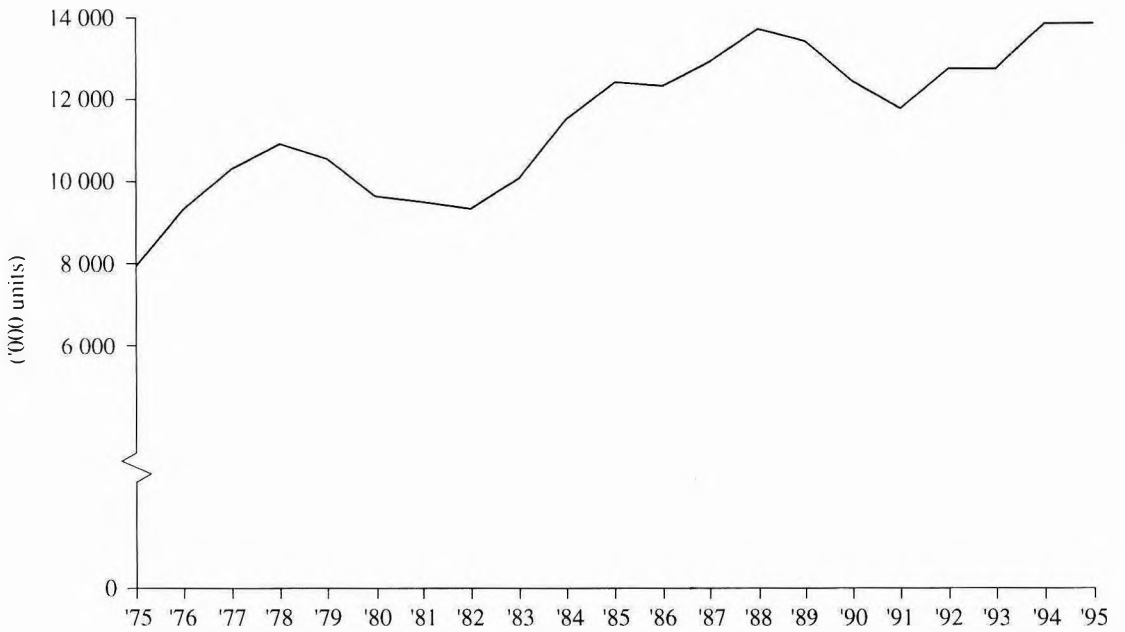


Figure 2. World CV production 1975 - 1995.

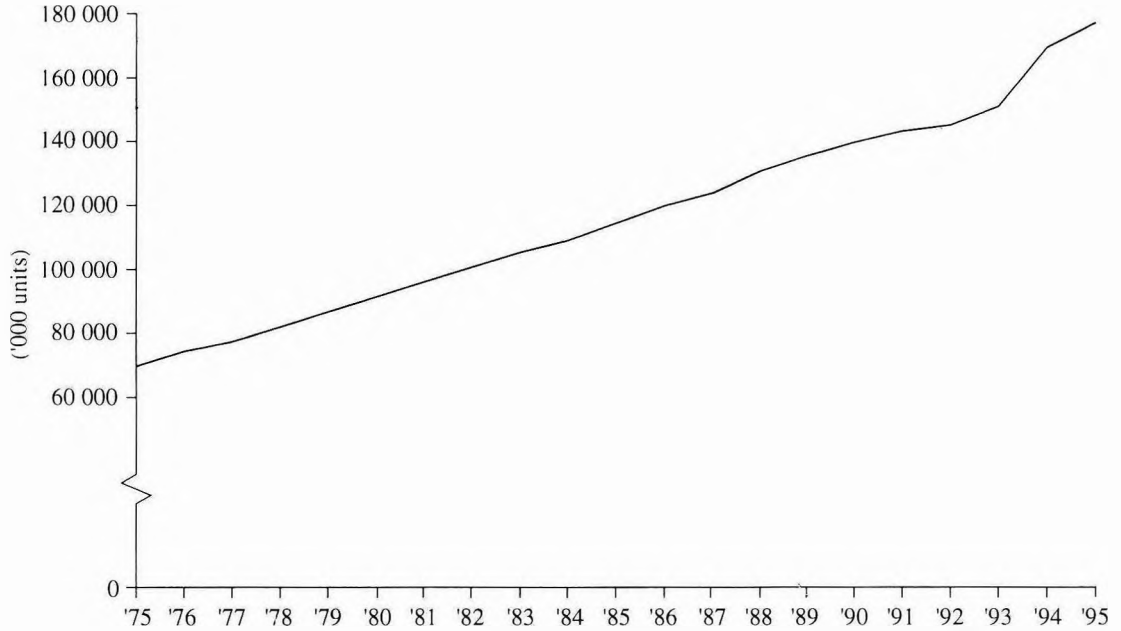


Figure 3. World CVs in use 1975 - 1995.

The level of production of LCV and HCV tyres differs from region to region, and is particularly important as this affects not only the levels of elastomer usage, but also the split between natural and synthetic rubber.

ELASTOMER CONTENT

In heavy-duty applications, considerable heat is generated in the shoulder area of the tyre between the casing and the tread and can lead to blow-out or to separation of the tread from the carcass. In this area of the tyre there is a high usage of natural rubber as its high resilience reduces heat build-up. Natural rubber/polybutadiene rubber blends can also provide

excellent wear characteristics coupled with good resistance to tread-groove cracking and rib tearing. For LCV tyres these considerations are less critical, and they use lower levels of natural rubber than HCV tyres. In general, the larger the truck tyre the higher the usage of natural rubber, with the large CV tyres using almost 90% natural rubber.

Currently (1995) there are some 240 million CV tyres (*Appendix 1*) being produced annually¹, of which some 62% or 150 million are LCV tyres.

During the 1980s it was assumed that the average HCV tyre used about 20 kg – 22 kg of

elastomers. The ratios of natural and synthetic rubber used in the production of cross-ply and radial-ply HCV tyres were 66:34 and 76:24, respectively (Bottasso, 1980). In the late 1980s, Carr *et al.*, using an elastomer content of 9–24 kg/tyre, estimated that truck tyres (including retreads) used about 24% of total rubber consumption.

The levels of natural and synthetic rubber vary considerably in the many different types of tyre. This is particularly important in assessing consumption in this market as the last 10–15 years have seen a very large growth in the production of tubeless radial LCV and HCV tyres, as well as low-profile radial HCV tyres. *Table 1* gives the estimated elastomer contents of truck tyres in western countries².

The average elastomer content has also been reported by Gelling and Newell³ for the tread and sidewall components of CV tyres from 1974–1990 (*Table 2*).

Baker⁴ has indicated that the sub-tread component of CV tyres is 80%–100% natural rubber, with bead stocks normally 100% natural rubber but with no natural rubber in innerliners.

Using the above information it may be assumed that the average HCV tyre contains 21 kg–28 kg of elastomers, of which about 70%–90% is natural rubber. Similarly, LCV tyres may be assumed to contain about 10 kg of elastomer, of which about 65% is natural rubber. Thus the estimated rubber consumption by CV tyres alone is shown in *Table 3*, which indicates that 47% of the world production of six million tonnes of natural rubber is used in CV tyres. HCV tyres, using some 1.8 million tonnes, are the largest single use of natural rubber⁵. This may have implications for the

movements in the natural rubber price (*Table 3*).

TRUCK TYRE DEVELOPMENTS

Industrialised Countries

The widespread use of radial-ply tyres began in Europe in the early 1960s and spread to North America and Japan 10–15 years later. The main advantage of radial CV tyres is in tyre life, which can be from 40% – 100% greater than that of a cross-ply tyre. In long-haul operations mainly on motorways, steering tyres can achieve 100–120 000 miles, drive tyres about 250–280 000 miles and trailer tyres about 130–150 000 miles before retreading, which can further extend tyre life. In addition, where motorways predominate, the lower rolling resistance of radials gives an improvement in fuel economy of 6%–10%.

The main driving forces behind the radialisation of truck tyres were changes in the design and loading of trucks, namely:

- Increased power—higher brake horsepower trucks and tractor units for sustained high speeds increases heat build-up leading to increased wear and fatigue;
- Loading—increased permitted weight per axle;
- Power steering—tighter and faster cornering; and
- Configuration—vehicle and trailer configurations giving inequalities in axle loading, again leading to increased wear.

The development of radial HCV tyres with lower rolling resistance has become a top

TABLE 1. ESTIMATED ELASTOMER CONTENT OF CV TYRES

	Rubber content (kg)	Natural rubber (%)
LCV tyres		
Conventional	4.5 – 8.5	31 – 68
Radial, tubed	5.0 – 8.5	40 – 89
Radial, tubeless	7.0 – 10.0	45 – 90
HCV tyres		
Conventional	21.0 – 23.5	52 – 73
Radial, tubed	21.5 – 27.0	69 – 87
Radial, tubeless	24.0 – 28.0	77 – 85
Radial, low profile	24.0 – 27.0	84 – 87

TABLE 2. ELASTOMER CONTENTS OF CV TYRE COMPONENTS

Year	Tread		Sidewall	
	NR	SR ^a	NR	SR ^a
1974	45	55	48	52
1981	60	40	44	56
1983	77	23	58	42
1985	86	14	62	38
1990	86	14	75	25

^aStyrene butadiene rubber (SBR) and polybutadiene, except in sidewalls in 1985 and 1990, when it was totally SBR.

priority for tyre manufacturers. With the continuing development of regrooving and multiple retreading, the life of HCV tyres is now approaching 400 000–600 000 miles. Like new tyres, retreads are becoming specialised relative to their axle position. In Europe the sales ratio of retread truck tyres to new tyres is about 1:1 in the replacement market, whereas in the USA this ratio rises to 1.4:1.

The development of low-profile CV tyres to reduce platform height and overall vehicle height while maintaining load capacity began in the mid-1980s and has continued in the 1990s. The larger rim diameters provide more space for the larger braking systems required with the elimination of asbestos brake liners. Other developments during the last 10 years have been the growth of tubeless tyres in both

TABLE 3. NATURAL RUBBER CONSUMPTION IN CV TYRES (MILLIONS OF TONNES: 1995)

	NR	SR	Total
LCV tyres	1.0	0.5	1.5
HCV tyres	1.8	0.5	2.3
Total	2.8	1.0	3.8

the LCV and HCV sectors, and the introduction of the wider 'super single' tyre to replace twin rear tyres. The super single tyre offers the advantage of reduced weight, reduced overall cost and better fuel economy. They are particularly advantageous for tanker truck operations because they allow the tank to be lower to the ground, giving a lower centre of gravity. However, with their smaller footprint on the road surface and high inflation pressure they cause greater road damage and in the case of deflation the truck cannot continue its journey.

Future changes in truck design and construction expected to influence future HCV tyre design are likely to include:

- Spread axles for laws relating to the load distribution on bridges;
- Twin-steer axles for increased load capacity, payload and improved truck/trailer configuration;
- Tandem spread axles with lift axles;
- Multiple tyre sizes for maximum cubic air capacity to support higher loads and to accommodate tri-axles;
- New vehicle designs with improved aerodynamics; and
- New tractor unit designs.

Other factors which may need to be considered by tyre manufacturers are:

- Pavement damage;
- Fuel economy developments;
- The development of larger road-trains and vehicle configurations; and
- Vehicle design coupled to changing legislation.

Developing Countries

These developments occurring in industrialised countries may not necessarily apply to continental Asia, Latin America and Africa, where the switch from cross-ply to radial-ply CV tyres has been very slow and much slower than predicted during the 1980s. Here, the local road, driving and loading conditions still favour the use of cross-ply tyres, which are suited to the poor road conditions since the more rigid sidewall is not as susceptible to damage under severe operating conditions caused by poor tyre maintenance, regular over-loading and constant kerbing. There appears to be little published information in the performance of radial truck tyres under these conditions, as most trials are conducted by tyre manufacturers for their own information. However, the results of a very small trial using steel radial precured first-life retreads has been published⁶. In India, six out

of ten retreads failed despite fitment to express buses to avoid overloading and poor road conditions. Four failures occurred below tyre-tread half-life, while two failed close to complete tread life at 59–60 000 km travelled. In Indonesia, eight out of ten retreads failed, although service conditions were again chosen to avoid overloading and use on poor roads. Four failures were below tyre half-life, but four failed only after travelling in excess of 100 000 km. In Malaysia, eight retreads travelled over 100 000 km without failures, although the condition of the casings would have precluded further retreading. The causes of radial retread failures are shown in *Table 4*.

Thus, it is evident that steel radial tyres are capable of providing high mileages, but the chances of premature failure are high and it is doubtful that retreading would be feasible, seriously affecting the economics of truck fleet operation.

It is anticipated that up to the year 2000, tubed conventional truck tyres will predominate in these areas as they are ideally suited to local conditions of overloading and poor road construction because of their lower susceptibility to carcass damage, especially of the sidewall. In these countries, future developments in the construction and design of conventional tyres are expected to include:

- Heavier ply gauges to protect against higher shear stresses;
- Extra chafers or thicker rubber skim to increase abrasion resistance and protect against rim digging due to overloading;
- Larger dimensions for increased air volume to improve load-carrying capability;

- Thicker sidewalls for better protection against cut/impact damage;
- The use of twin bead construction in place of a single bead; and
- More robust shoulder ribs.

However, the majority of investments being announced by the major tyre companies in developing countries relates to radial tyre production. These tyres may initially be intended for the export market to reduce production costs.

FUTURE PROJECTIONS OF CONSUMPTION IN CV TYRES

A recent report by the Economist Intelligence Unit (EIU)⁷ has indicated that the production of CV tyres will increase to about 270 million units in the year 2000 and rise to nearly 315 million units in the year 2005. Given the tyre developments referred to in the section under Truck Tyre Developments, it is anticipated that not only will there be an absolute increase in the usage of natural rubber in CV tyres due to increased production, but also that the proportionate usage relative to synthetic rubber will rise. Thus it is envisaged in 2005 that HCV tyre production will be in the order of 125 million units (with LCV — 190 million units), with an average elastomer content of nearly 90% natural rubber (LCV — 70%). Therefore the usage of natural and synthetic rubber in CV tyres only is estimated in *Table 5*.

In the case of natural rubber the main source of the absolute increase in consumption is to be derived from the additional one million tonnes usage by HCV tyres.

TABLE 4. STEEL RADIAL PRECURED RETREAD FAILURES

Distance travelled (km)	Cause of failure
	India
23 486	Shoulder damage: penetration
26 675	Sidewall crack: impact penetration
27 787	Sidewall cut: stone impact
30 323	Sidewall cut: impact
58 136	Sidewall failure: impact
63 171	Crown penetration
	Indonesia
6 850	Sidewall break-up: concussion
15 160	Sidewall damage: impact
15 520	Casing break-up: under-inflation?
39 726	Sidewall damage: impact
>105 000	Sidewall damage: impact
>105 000	Sidewall damage: concussion
>105 000	Sidewall cracking: fatigue?
>105 000	Sidewall damage

TABLE 5. NATURAL RUBBER CONSUMPTION IN CV TYRES (MILLIONS OF TONNES: 2005)

	NR	SR	Total
LCV tyres	1.2	0.7	1.9
HCV tyres	2.8	0.3	3.1
Total	4.0	1.0	5.0

Recent estimates by the IRSG Secretariat indicate that the total world elastomer demand in 2005 is likely to reach 23 million tonnes, of which natural rubber's share will be about 40% or 9 million tonnes⁸. Thus the share of CV

tyres in natural rubber consumption is expected to remain roughly constant at around 45%, with HCV tyres continuing to provide the major outlet accounting for some 30% of total world natural rubber consumption.

HCV TYRE SALES AND THE NATURAL RUBBER PRICE

Although the natural rubber price undoubtedly moves in cycles related to the world economy, there are 'spike' movements, whereby in a few months it moves dramatically downwards or upwards. Such spikes occur at the beginning and end of cycles of world economic prosperity. As noted above, HCV tyres represent the largest single use of natural rubber, currently accounting for 30% of total natural rubber consumption. It therefore appears possible that major fluctuations in HCV tyre demand — and hence production — might have a detectable influence on the natural rubber price. One possible cause of such fluctuations has been identified in the use by transport fleet operators of wheels from trailers made redundant by reduced demand during the lead-in to an economic recession to replace worn tyres on those units still in use.

Although retreaded tyres are often used on trailers, there will in these circumstances be increased economic pressure to reduce the purchases of new tyres in this way. When the next economic upturn occurs, there may be a higher demand for truck tyres for the 'hibernating' trailers to bring them back into use. This could rapidly increase the demand for both new and retreaded HCV tyres. Work is currently under way using data provided by the major rubber manufacturers' associations to examine whether changes in truck tyre demand may be a major 'fundamental' in the demand — and hence the price — of natural rubber⁹.

CONCLUSIONS

Natural rubber is an essential component in the manufacture of LCV and HCV truck tyres,

especially those of radial-ply construction. Over the past 20 years the use of natural rubber in truck tyres has increased slowly in percentage terms, but significantly in absolute volume. This has been primarily due to the increasing penetration of radial technology for truck tyres and the development of tubeless and low-profile LCV and HCV tyres. In radial HCV tyres, which can be retreaded two or three times, natural rubber content may be as high as 90%.

The emphasis of truck tyre development over the last 10 years has been primarily on economy, which has been based on low rolling resistance, wear resistance and retreadability. These may continue to be the priorities for the future although lower tyre weights, reduced irregular wear, lower noise levels and lower heat build-up may also become more important.

With regard to the usage of elastomers in truck tyres over the next few years, the following aspects should be important:

- Natural rubber will continue to be used in large quantities in most components in a truck tyre;
- Sidewalls will still use natural-synthetic rubber blends, although future developments may encourage the usage of synthetic rubber, and
- New CV tyre retread components will continue to use high levels of natural rubber, whether the tyre is used in a steering, driving or trailer position, but synthetic rubber will continue its dominance of the retread market.

It is future developments in the construction of trucks in the western world and the development of improved road systems in Asia,

Latin America and Africa that will increase the radialisation of CV tyres. As world economies continue to develop this will provide the future growth in derived demand for natural rubber from the manufacture of truck tyres, which will remain the largest market for natural rubber at about 45% of the total, with HCV tyres alone continuing to account for around 30% of world natural rubber consumption.

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APPENDIX I. COMMERCIAL VEHICLE TYRE PRODUCTION ('000 UNITS)

Year	Other										German							
	Canada	USA	Argentina	Brazil	Chile	Colombia	Mexico	Venezuela	Latin America	Austria	Benelux	Finland	France	Germany	DR	Greece	Italy	Portugal
1975	2,529	28,611	1,190	2,752	57	378	1,913	801	500	500	762	36	4,935	3,468	2,071	230	2,886	314
1976	3,299	29,474	1,324	3,037	151	408	2,240	821	600	550	696	27	5,131	3,724	2,123	240	2,798	293
1977	3,327	38,199	1,416	3,422	204	377	2,188	880	650	600	827	30	5,404	4,044	2,195	250	2,762	409
1978	3,200	40,226	1,298	3,505	191	547	2,884	927	750	640	851	115	5,736	3,883	2,220	275	2,734	510
1979	3,357	38,659	1,532	3,506	223	451	3,138	1,033	800	755	977	110	6,366	4,242	2,274	300	2,894	510
1980	3,325	28,402	1,440	3,942	232	513	3,520	1,045	850	825	1,070	115	6,182	4,220	2,332	340	2,794	560
1981	2,895	31,973	1,041	4,161	217	460	3,510	990	750	730	1,096	130	5,360	3,977	2,319	430	2,570	650
1982	2,873	29,019	537	6,300	120	472	4,610	930	850	620	981	140	4,049	3,558	2,327	450	2,370	570
1983	3,432	30,667	1,064	6,494	150	486	6,540	900	950	630	1,064	160	4,427	3,757	2,435	280	2,330	620
1984	4,198	36,441	810	5,624	228	526	4,330	896	1,000	825	1,077	165	5,460	3,805	2,570	315	2,847	460
1985	4,135	34,339	1,190	5,182	216	540	4,870	1,350	1,100	595	1,169	246	4,249	3,970	2,760	340	2,795	502
1986	3,980	30,939	1,400	7,170	216	567	5,350	1,505	1,250	560	1,254	220	5,499	4,023	2,823	365	2,805	584
1987	3,904	35,455	1,690	9,924	306	580	5,600	1,634	1,370	560	1,339	215	5,590	4,192	2,891	350	2,974	671
1988	2,468	37,010	1,970	7,681	333	594	6,000	1,562	1,440	550	1,608	190	5,801	5,017	2,919	530	2,946	644
1989	2,927	37,844	1,689	8,069	390	567	3,995	1,253	1,460	540	1,747	220	6,083	5,366	2,930	350	3,027	640
1990	2,694	35,804	1,736	7,868	408	553	4,989	1,203	1,290	570	1,766	200	5,858	5,475	1,620	300	2,933	471
1991	2,646	32,811	1,400	8,260	456	460	5,408	1,433	1,440	650	1,809	370	5,799	5,980		290	2,752	600
1992	2,842	37,525	1,730	8,806	500	480	5,139	1,416	1,590	530	1,920	255	5,928	6,331		150	2,679	620
1993	3,363	39,927	1,790	6,170	550	440	4,736	1,644	1,760	480	1,900	375	5,143	5,187		130	2,367	650
1994	3,755	42,264	1,711	6,670	571	460	5,396	1,628	1,790	500	2,030	360	5,713	4,855		140	2,500	863
1995	4,448	45,027	1,782	7,070	583	440	4,952	1,620	1,810	580	2,140	350	5,925	6,065		140	3,030	900

APPENDIX 1. COMMERCIAL VEHICLE TYRE PRODUCTION ('000 UNITS) (CONTD)

Year	Spain	Sweden	UK	Bulgaria	Czech Rep.	Hungary	Norway	Poland	Romania	Russian Fed.	Slovak Rep.	Slovenia	Switzerland	Turkey	F.R. of Yugoslavia	Other Europe	South Africa	Other Africa
1975	2,111	213	3,790	417	1,494	670	10	2,749	1,926	20,469			5	713	582		1,429	1,000
1976	1,950	123	3,825	420	1,519	688	10	2,543	2,140	21,676			5	740	643		1,274	1,050
1977	2,180	183	3,665	449	1,636	706	15	2,371	2,217	22,822			5	742	925		1,311	1,100
1978	2,496	155	3,499	425	1,669	663	15	2,085	2,390	23,466			10	913	1,010		1,415	1,100
1979	2,749	185	3,285	429	1,694	650	20	2,400	2,413	23,849			10	870	1,043		1,398	1,150
1980	2,843	156	3,447	521	1,739	655	25	2,502	2,602	23,882			10	999	1,091		1,519	1,200
1981	2,800	82	2,895	533	1,784	615	25	1,741	2,693	24,045			10	815	1,197		1,838	1,250
1982	2,031	83	2,418	536	1,577	549	25	1,550	2,804	24,057			10	985	1,069		1,782	1,300
1983	1,965	59	2,249	543	1,562	732	25	1,917	2,780	24,520			10	1,298	1,073		1,503	1,300
1984	2,420	84	2,422	567	1,617	792	40	1,039	3,059	24,647			15	1,488	1,124		1,659	1,350
1985	2,930	105	2,294	564	1,651	825	49	2,221	2,013	26,104			20	1,670	1,283		1,479	1,400
1986	2,511	110	2,329	567	1,671	857	50	2,143	2,235	26,375			20	1,767	1,148		1,590	1,400
1987	2,769	115	2,539	631	1,711	888	50	1,993	1,857	26,906			20	1,688	1,005		1,712	1,450
1988	3,127	118	2,668	576	1,789	903	40	2,078	1,919	27,326			18	1,635	937		1,949	1,450
1989	3,344	116	2,972	599	1,849	967	35	1,960	1,840	27,517			17	1,417	1,072		1,997	1,500
1990	2,975	19	2,782	598	1,819	855	20	1,129	1,267	26,317			19	1,114	1,026		2,270	1,500
1991	2,872	31	2,839	382	1,662	612	-	1,800	890	25,181			10	2,038	503		1,875	1,550
1992	3,029	169	2,479	353	2,154	516	-	1,810	862	16,919		1,447	7	1,683	194	4,900	2,141	1,450
1993	2,989	169	3,084	266	2,150	441	-	1,700	733	13,470	660	1,529	-	1,792	78	4,000	1,501	1,500
1994	3,249	69	3,222	187	1,270	508	-	2,100	691	7,244	1,150	1,621	-	1,528	143	2,500	1,551	1,550
1995	3,558	120	3,349	218	1,820	660	-	2,700	774	6,333	1,644	977	-	1,658	114	3,000	1,729	1,600

APPENDIX I. COMMERCIAL VEHICLE TYRE PRODUCTION ('000 UNITS)

Year	Aust- ralia	China	India	Indonesia	Iran	Israel	Japan	Rep. of Korea	Malaysia	New Zealand	Pakistan	Philip- pines	Sri Lanka	Taiwan	Thailand	Other Asia	World Grand Total
1975	577	5,950	2,880	1,006	600	293	25,782	1,363	500	200	120	794	...	639	900	400	133,500
1976	649	5,860	2,724	1,678	500	336	28,199	1,559	633	230	100	637	...	701	867	450	140,700
1977	679	6,221	3,069	2,339	550	344	31,113	1,854	725	230	110	797	...	730	1,066	500	157,800
1978	595	6,837	3,410	2,540	600	308	33,446	2,604	689	240	110	889	...	1,035	1,141	500	166,700
1979	645	7,713	3,473	2,898	400	263	38,866	3,179	692	240	115	958	...	773	1,276	550	175,300
1980	534	7,627	3,707	2,051	600	248	46,133	2,790	688	250	120	883	...	847	1,167	550	173,100
1981	597	6,061	3,825	2,242	500	221	44,572	4,906	798	240	110	879	...	874	1,547	550	173,500
1982	493	6,567	4,340	2,859	600	217	42,272	3,764	652	240	100	1,006	...	966	1,363	550	167,500
1983	475	8,055	4,449	2,401	650	209	46,368	4,642	663	190	100	1,100	...	1,300	1,610	600	180,700
1984	470	9,220	4,613	2,501	700	202	48,287	5,699	696	220	125	950	...	2,093	1,790	600	192,100
1985	480	10,559	4,680	2,880	621	190	48,259	6,296	568	204	138	850	23	2,361	1,221	600	194,100
1986	880	10,550	4,933	3,251	537	149	44,009	8,420	525	168	130	588	80	1,340	1,244	600	192,700
1987	1,070	12,090	4,170	3,343	688	185	45,518	9,160	672	215	181	724	85	1,560	1,580	650	206,500
1988	1,150	14,315	5,569	4,360	668	115	49,879	10,531	811	130	272	1,218	78	1,840	2,057	650	219,400
1989	1,200	15,152	5,809	5,199	721	151	50,003	10,319	895	140	317	1,216	77	1,931	2,250	700	222,400
1990	1,250	13,862	5,989	5,874	962	156	49,656	11,791	1,044	120	333	1,308	103	2,131	1,737	700	216,500
1991	1,200	17,292	6,015	6,128	847	157	48,997	13,819	1,438	120	274	1,100	101	1,849	1,924	750	216,800
1992	1,250	22,229	6,533	6,191	1,003	178	46,562	14,856	1,370	130	249	1,400	81	1,609	2,212	800	225,200
1993	1,250	29,317	6,662	6,853	996	171	41,357	14,680	1,460	140	274	1,550	44	1,340	2,544	850	222,200
1994	1,300	32,099	7,554	8,142	1,308	193	40,812	15,520	1,539	150	288	1,700	80	1,140	2,900	850	225,400
1995	1,350	32,134	8,629	9,227	1,200	184	44,531	16,514	1,596	160	351	1,600	95	850	3,600	900	240,000

Source: World Rubber Statistics Handbook Vol. 5

Figures in bold italics are estimates

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