

# Rheological properties of ethylene propylene diene rubber (EPDM) compound – effect of blowing agent, curing agent and carbon black filler

Krishna Ch. Guriya, A. K. Bhattachariya and D. K. Tripathy\*

Rubber Technology Centre, Indian Institute of Technology,

Kharagpur-721302, Kharagpur, India

(Revised 28 February 1997)

An experimental investigation has been carried out to study the rheological behaviour of ethylene propylene diene rubber (EPDM) compounds in extrusion containing blowing agent. The cell morphology development and rheological properties have been studied for gum and carbon black filled systems with variation of the blowing agent, extrusion temperature and shear rate. The apparent shear stress ( $\tau_{wa}$ ), apparent viscosity ( $\eta_a$ ), die swell (%) and total extrusion pressure ( $\Delta P$ ) of the carbon black filled EPDM rubber compounds have been determined using the Monsanto processability tester (MPT). The effect of the curing agent and blowing agent (DNPT) on the rheological properties of the compound has also been studied. There is a significant reduction in stress and viscosity with the blowing agent in the presence of curing agent compared with the absence of curing agent. The viscosity reduction factor is found to be dependent on the blowing agent loading, shear rate and temperature.

© 1997 Elsevier Science Ltd.

(Keywords: rheological properties; blowing agent; curing agent)

## INTRODUCTION

The use of physical and chemical blowing agents in producing elastomeric foams has been practised for several years. Under usual processing conditions the physical and chemical blowing agents influence the rheological properties of the compounded elastomers. Extrusion of material containing blowing agent is an important industrial processing operation<sup>1,2</sup>. Future improvements in these processes may well depend on a better understanding of the processes and mechanisms involved. Studies of bubble morphology development and apparent rheological properties of thermoplastics in foam extrusion processes and the effect of processing variables on the quality of foam produced have been reported by several authors<sup>3–5</sup>. An important aspect of foam extrusion is the mechanics of bubble growth in the polymer matrix. Numerical and experimental studies of bubble growth during the microcellular foaming process and the influence of temperature, saturation pressure, molecular weight, and the nature of physical blowing agent have been reported recently<sup>6</sup>. Shear effects on thermoplastic foam nucleation have been studied on a twin screw foam extruder<sup>7</sup>. Several rheological aspects of thermoplastic foam extrusion have been described by a phenomenological model of the flow in an extrusion die<sup>8</sup>. A few experimental studies of bubble growth in elastomers are also found in the literature<sup>9–11</sup>. Recently, bubble growth and physical properties of thermoplastic elastomers have also been reported with respect to extrusion foaming<sup>12</sup>. Extensive studies have been carried out dealing with the rheological properties of homopolymers in the molten

state, polymer blends and filled polymers<sup>13</sup>. A few reports are available which deal with the rheological properties of mixtures of molten polymer and blowing agent (physical and chemical)<sup>14,15</sup>. When a blowing agent is added to a rubbery mix to produce a microcellular rubber, several phenomena can influence the extrusion behaviour of the mixture. The blowing agent will also affect the rheological behaviour of the compounds.

In the present study, the rheological properties of ethylene propylene diene rubber (EPDM) compound with variation of blowing agent loading in both gum and carbon black filled systems have been studied. The effect of temperature in extrusion has also been investigated. The morphological studies of the extrudate are performed to characterize the cellular structure of the extrudate.

## EXPERIMENTAL DETAILS

### Materials

The EPDM rubber (Kelton 520, ethylene content 55 mol%, diene content 4.5 mol% (DCPD), specific gravity 0.86, manufactured by DSM chemicals, Holland) was used. HAF black (N330) was used as filler, manufactured by Phillips Carbon Black, India. The dicumyl peroxide (DCP) used was Percidol 540C (40% DCP on inert filler), manufactured by Chemoplast(I) Ltd. Dinitrosopentamethylene tetramine (DNPT) used as blowing agent was manufactured by High Polymer Labs, India.

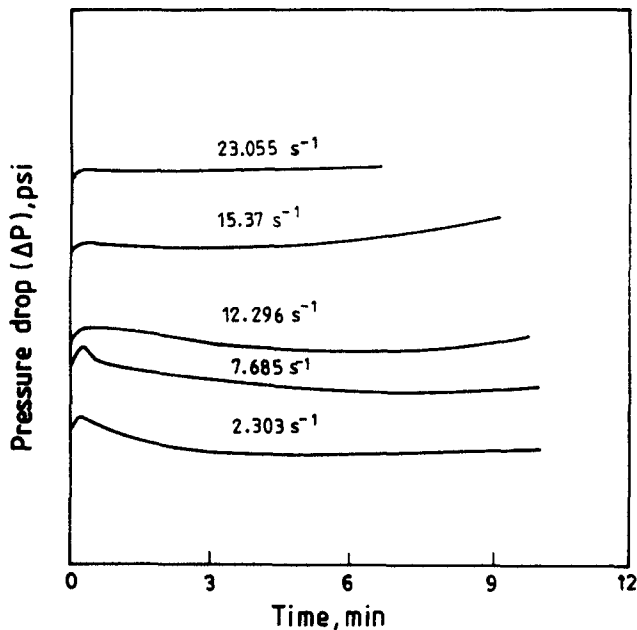
### Compounding

The rubber was compounded with other ingredients according to the formulations of the mixes (Table I) in a two-roll mill and the blowing agent was added at the end.

\* To whom correspondence should be addressed.

**Table 1** Formulations of the mixes

	G <sub>1</sub>	G <sub>2</sub>	G <sub>3</sub>	G <sub>4</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>
EPDM	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	2	2	2	2	2	2	2	2	2	2	2	2
St. acid	2	2	2	2	2	2	2	2	2	2	2	2
P. oil	2	2	2	2	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Carbon black	—	—	—	—	30	30	30	30	30	30	30	30
DCP	—	2	—	2	—	2	—	—	—	2	2	2
DNPT	—	—	2	2	—	—	2	4	6	2	4	6



**Figure 1** Representative curve for pressure drop  $\Delta P$  versus time plots with variation of shear rate

*Measurement of rheological properties*

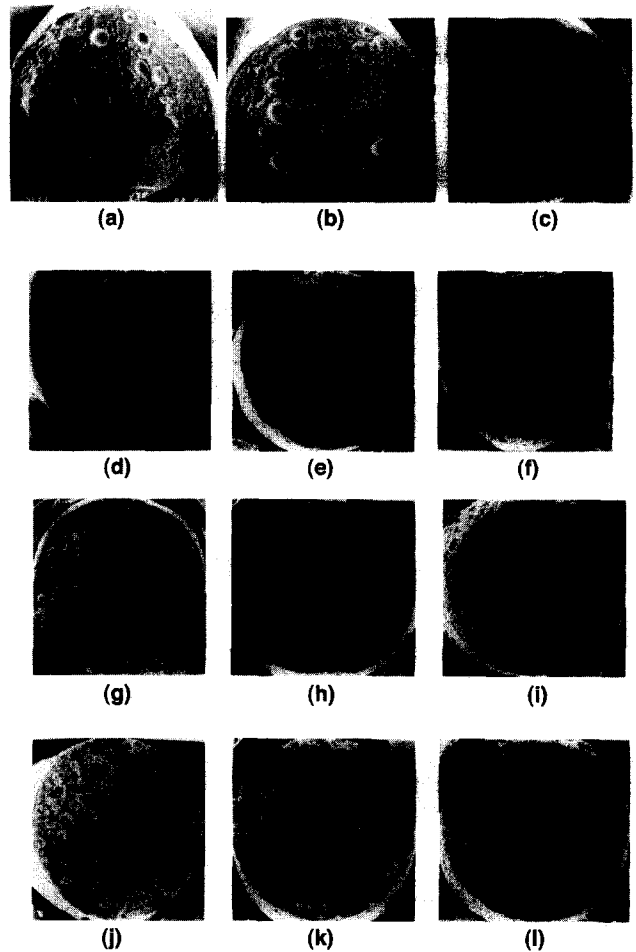
Rheological properties of the samples have been studied with the help of a Monsanto processability tester (MPT, No. 83077). The capillary used is 2 mm in diameter having a length to diameter ratio ( $L/D$ ) equal to 16:1. The test sample was charged into the barrel and preheated for 3 min for uniform temperature distribution and was extruded with different piston rates (0.02, 0.05, 0.08, 0.10, 0.15 inch  $\text{min}^{-1}$ ) with time. These piston rates correspond to the apparent wall shear rates ( $\dot{\gamma}_{wa}$ ) 3.074, 7.685, 12.296, 15.37 and 23.055  $\text{s}^{-1}$  respectively. The representative plots of pressure drop over the capillary ( $\Delta P$ ) against extrusion time are shown in *Figure 1*. From the values of plots the pressure drop apparent shear stresses are calculated for different extrusion times.

The apparent wall shear rate  $\dot{\gamma}_{wa}$  and apparent wall shear stress  $\tau_{wa}$  are calculated from knowledge of the barrel diameter, piston speed, length and diameter of the capillary. These are expressed as

$$\tau_{wa} = \frac{d\Delta P}{4l} \tag{1}$$

$$\dot{\gamma}_{wa} = \frac{32Q}{\pi d^3} \tag{2}$$

where  $\tau_{wa}$  is the shear stress at the wall,  $d$  is the capillary diameter,  $l$  is the capillary length.  $\Delta P$ , the pressure drop over



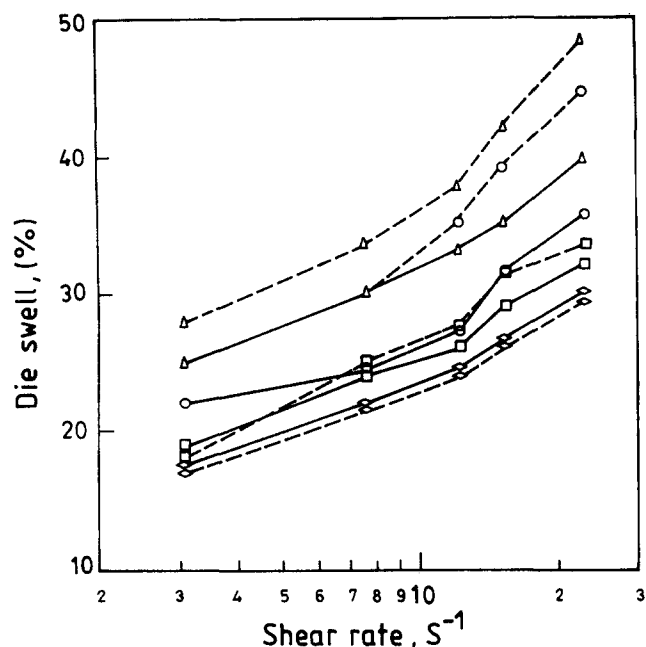
**Figure 2** SEM photomicrographs of gum and carbon black filled extrudates at 35 × magnification: (a) G<sub>3</sub>, 3.074  $\text{s}^{-1}$ , 140°C; (b) G<sub>3</sub>, 23.055  $\text{s}^{-1}$ , 140°C (c) G<sub>4</sub>, 23.055  $\text{s}^{-1}$ , 140°C; (d) C<sub>3</sub>, 12.296  $\text{s}^{-1}$ , 140°C; (e) C<sub>5</sub>, 12.296  $\text{s}^{-1}$ , 140°C; (f) C<sub>3</sub>, 12.296  $\text{s}^{-1}$ , 150°C; (g) C<sub>5</sub>, 12.296  $\text{s}^{-1}$ , 150°C; (h) C<sub>6</sub>, 12.296  $\text{s}^{-1}$ , 140°C; (i) C<sub>7</sub>, 12.296  $\text{s}^{-1}$ , 140°C; (j) C<sub>8</sub>, 12.296  $\text{s}^{-1}$ , 140°C; (k) C<sub>7</sub>, 3.074  $\text{s}^{-1}$ , 150°C; (l) C<sub>7</sub>, 23.055  $\text{s}^{-1}$ , 150°C

the capillary length, is measured as a pressure gauge reading at the inlet of the capillary.  $\dot{\gamma}_{wa}$  is the apparent rate of shear at the wall,  $Q$  is the volumetric flow rate of the compounded material.

The apparent shear viscosity is given by the relation

$$\eta_a = \frac{\tau_{wa}}{\dot{\gamma}_{wa}} \tag{3}$$

The running die swell (the die swell at the exit of the die as soon as the extrudate comes out) data have been directly recorded with the help of an in-built laser scanning system.



**Figure 3** Die swell (%) versus shear rate plots of gum compounds at different temperatures after 3 min extrusion: (—) 140°C; (---) 150°C; G<sub>1</sub> (◇); G<sub>2</sub> (○); G<sub>3</sub> (□); G<sub>4</sub> (△)

#### Scanning electron microscopy (SEM)

SEM photomicrographs of razor cut surfaces of micro-cellular extrudate were obtained using a Cam Scan series 2 model scanning electron microscope. The surface of the samples was gold coated using a vacuum gold sputter machine for the SEM studies.

## RESULTS AND DISCUSSION

#### Morphology of gum and carbon black filled extrudate

The effect of blowing agent, curing agent, shear rate and temperature on the cell size of the extrudates is shown in the SEM photomicrographs (Figure 2). The formation of gas bubbles that occur inside the capillary depends on the pressure, temperature, type and concentration of blowing agent. The average cell size of the extrudate with variation

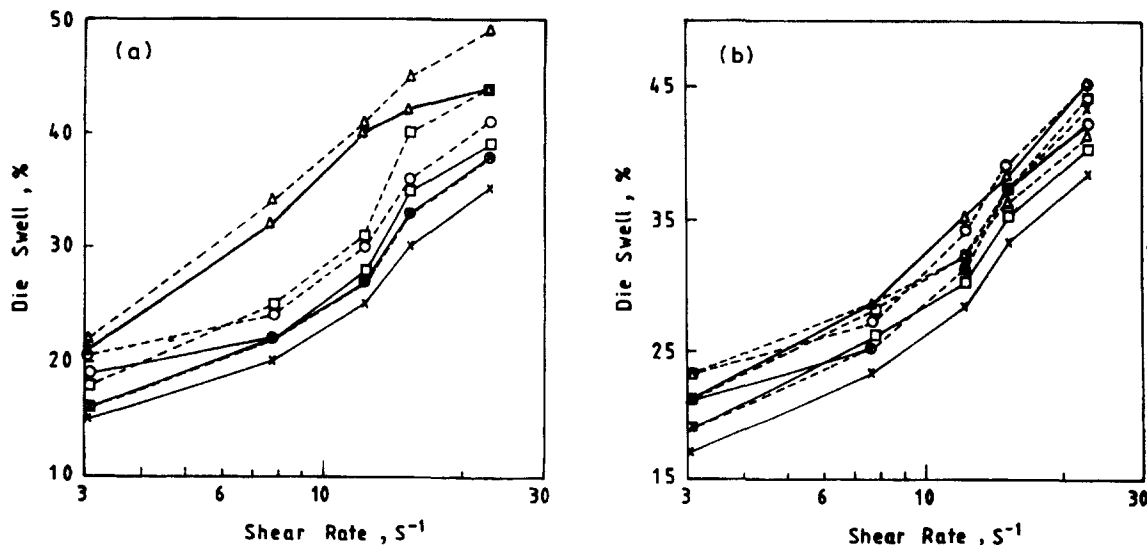
**Table 2** The average cell size of the extrudate with variation of shear rate, temperature and loading of blowing agent

Mix	Shear rate (s <sup>-1</sup> )	Temperature (°C)	Average cellsize (μm)
G <sub>3</sub>	3.074	140	261.87
G <sub>3</sub>	23.055	140	196.69
G <sub>4</sub>	23.055	140	172.16
C <sub>3</sub>	12.296	140	54.54
C <sub>5</sub>	12.296	140	82.06
C <sub>3</sub>	12.296	150	109.09
C <sub>5</sub>	12.296	150	81.81
C <sub>6</sub>	12.296	140	76.35
C <sub>7</sub>	12.296	140	88.74
C <sub>8</sub>	12.296	140	115.62
C <sub>7</sub>	3.074	150	92.72
C <sub>7</sub>	23.055	150	114.53

of shear rate, temperature and loading of blowing agent is shown in Table 2. It is observed that with an increase in shear rate the number of cells increases in gum compounds in the absence of curing agent with smooth skin (Figure 2(a,b)). The cell sizes of the extrudate are more or less spherical in nature. In the presence of curing agent the number of cells increases (Figure 2(c)). With an increase in blowing agent loading in carbon black filled compounds the average cell size increases and the number of cells increases for any shear rate at 140°C (Figure 2(d,e)) and 150°C (Figure 2(f,g)) in the absence of curing agent. The cell sizes of the filled extrudate are found to be non-spherical in nature. In the presence of curing agent the cell size decreases and the cells are uniformly distributed in the matrix at 140°C (Figure 2(h-j)). The addition of curing agent increases the viscosity of the compounds and thus the dissolved gases are unable to escape from the mass. Also with increase in shear rate the number of cells increases and the average cell size of carbon black filled compound decreases (Figure 2(k,l)) at 150°C in the presence of curing agent. With the increase in temperature the number of cells also increases at any shear rate (Figure 2(d,f)).

*Die swell: effect of blowing agent and curing agent in gum and carbon black filled compounds at different temperatures*

The die swell of gum compounds at 140°C and 150°C is



**Figure 4** Die swell (%) versus shear rate plots of carbon black filled compounds at different temperatures after 3 and 6 min extrusion: (a) 140°C; (b) 150°C; (—) 3 min; (---) 6 min; C<sub>1</sub> (×); C<sub>2</sub> (○); C<sub>3</sub> (□); C<sub>6</sub> (△)

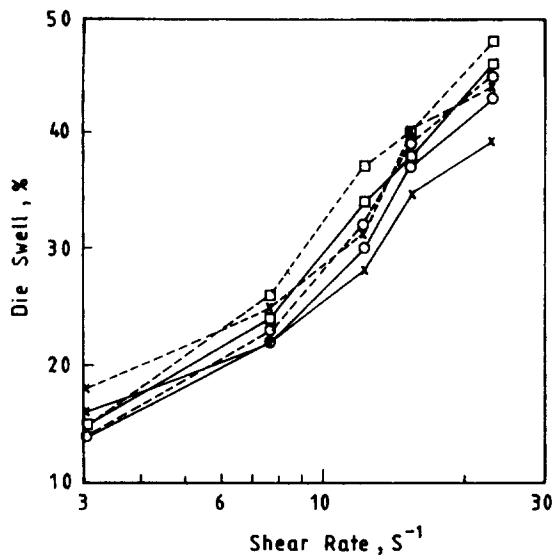


Figure 5 Die swell (%) versus shear rate plots of carbon black filled compounds with variation of blowing agent loading without curing agent at 140°C: (—) 3 min; (- - -) 6 min; C<sub>3</sub> (×); C<sub>4</sub> (○); C<sub>5</sub> (□)

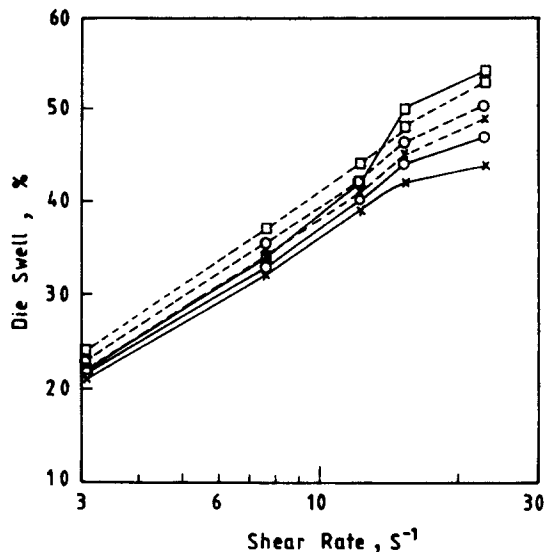


Figure 6 Die swell (%) versus shear rate plots of carbon black filled compounds with variation of blowing agent loading with curing agent at 140°C: (—) 3 min; (- - -) 6 min; C<sub>6</sub> (×); C<sub>7</sub> (○); C<sub>8</sub> (□)

shown in Figure 3 after 3 min extrusion time. The figure demonstrates that for the gum compound the die swell increases with shear rate and with decreasing temperature. On addition of blowing agent and curing agent, the die swell increases with shear rate and temperature. The rate of increase is more appreciable at higher shear rate.

The die swells of carbon black filled compounds at 140°C and 150°C are shown in semilogarithmic plots (Figure 4(a,b)) after 3 and 6 min extrusion time. Both curing agent and blowing agent enhance the die swell at 140°C and 150°C compared to base compound. In the presence of curing agent, the rate of increase in the die swell for the compounds with blowing agent is higher than that in the absence of curing agent. However, at higher shear rate, the rate of increase in the die swell decreases. With increase in the shear rate the die swell increases in all cases. At higher shear rate, the rate of increase in the die swell is less in the presence of both curing and blowing agent. In the presence

of curing agent the skin breaks down at higher shear rate leading to release of the decomposed gas from the system. This may be the cause of the decrease in die swell. Figure 5 demonstrates the die swell of carbon black filled compounds with the variation in blowing agent loading without curing agent after 3 and 6 min extrusion time at 140°C. The die swell increases with the increase in both blowing agent loading and extrusion time. The effect of blowing agent loadings in the presence of curing agent is shown in Figure 6 at 140°C. The relative difference in the die swell of the compounds with both curing agent and blowing agent at low shear rate is not that significant as compared to that at the higher shear rate. The effect of blowing agent loading at higher temperature (150°C) in the presence as well as absence of curing agent shows a similar trend and is hence not reported.

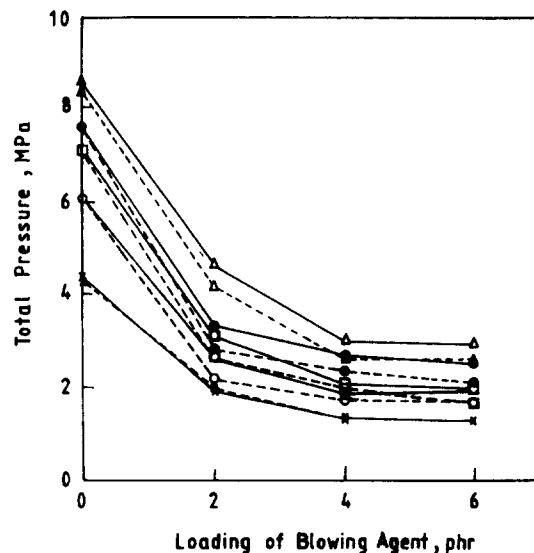


Figure 7 Total extrusion pressure of carbon black filled compounds as a function of blowing agent loading at various shear rates and different extrusion times without curing agent at 140°C: (—) 3 min; (- - -) 6 min; (×) 2.303 s<sup>-1</sup>; (○) 7.685 s<sup>-1</sup>; (□) 12.296 s<sup>-1</sup>; (Δ) 15.37 s<sup>-1</sup>; (●) 23.055 s<sup>-1</sup>

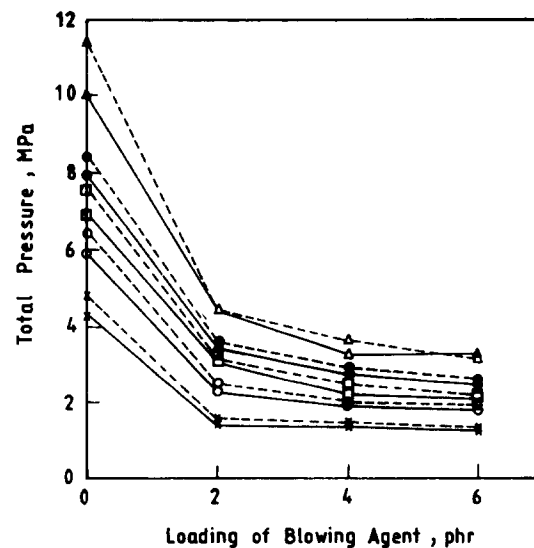


Figure 8 Total extrusion pressure of carbon black filled compounds as a function of blowing agent loading at various shear rates and different extrusion times with curing agent at 140°C: (—) 3 min; (- - -) 6 min; (×) 2.303 s<sup>-1</sup>; (○) 7.685 s<sup>-1</sup>; (□) 12.296 s<sup>-1</sup>; (Δ) 15.37 s<sup>-1</sup>; (●) 23.055 s<sup>-1</sup>

### Total extrusion pressure

The total extrusion pressure drop of carbon black filled compounds is plotted as a function of blowing agent loading at various shear rate and extrusion time at a temperature of 140°C in Figures 7 and 8. The total pressure drop decreases with increase in blowing agent loading at any shear rate, extrusion time and temperature. The decrease in total pressure drop is more for higher extrusion time owing to greater decomposition of blowing agent. Incorporation of the blowing agent causes a sharp decrease in the pressure initially followed by a slow decrease with increase in the blowing agent loading. The decomposition of the blowing agent is responsible for the initial decrease in pressure drop. However with an increase in blowing agent loading the change in pressure drop is not so effective. The initial pressure drop is more for the compound containing both blowing agent and curing agent (Figure 8) at 140°C. The higher reduction of the total extrusion pressure drop is due to the effective entrapment of decomposed gas in the presence of curing agent.

### Stress behaviour

Effect of blowing agent and curing agent of the compounds at different extrusion time. Figure 9 shows the

logarithmic plots of apparent shear stress ( $\tau_{wa}$ ) versus apparent shear rate illustrating the effect of curing agent and blowing agent on gum compounds after 3 and 6 min extrusion at 140 and 150°C. Figure 9(a,b) show the gradual increase in the shear stress with the increase in the shear rate. The compound without the curing agent and the blowing agent (gum compound) follows the power law irrespective of change in temperature and extrusion time. The compounds containing either the blowing agent or curing agent or both show a non-linear relationship between shear stress and shear rate. The presence of only blowing agent in the compound restricts the stress rise with the shear rate irrespective of the temperature and the extrusion time. The retardation in stress rise at high shear rate is due to the decomposition of the blowing agent. The decomposition of blowing agent produces gas bubbles which dissolves in the mass or form microbubbles and hence restrict the stress rise. However, in the presence of both the curing and the blowing agents, the decomposed gas is unable to release from the compound which restricts the increase in shear stress with shear rate compared to the compound containing only curing agent.

Figure 10 shows the logarithmic plots of apparent shear stress ( $\tau_{wa}$ ) versus apparent shear rate illustrating the effect

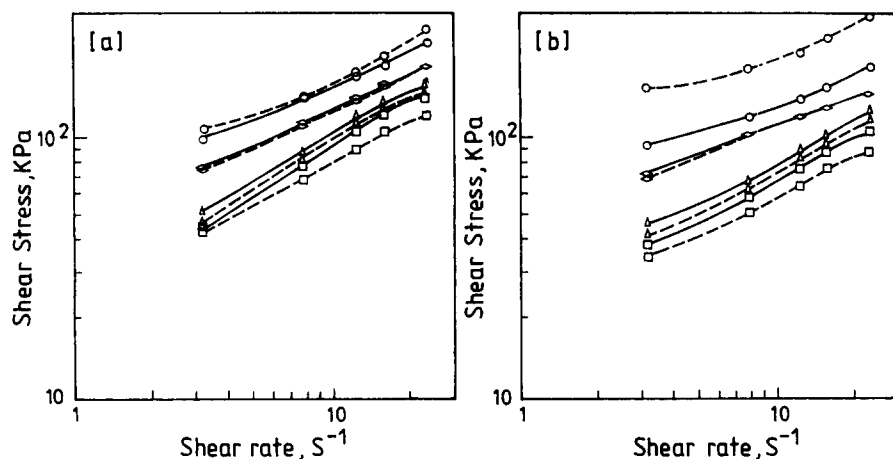


Figure 9 Apparent shear stress versus apparent shear rate plots of gum compound showing the effect of blowing agent and curing agent at different temperatures and after 3 and 6 min of extrusion time: (a) 140°C; (b) 150°C; (—) 3 min; (---) 6 min; G<sub>1</sub> (◇); G<sub>2</sub> (○); G<sub>3</sub> (□); G<sub>4</sub> (△)

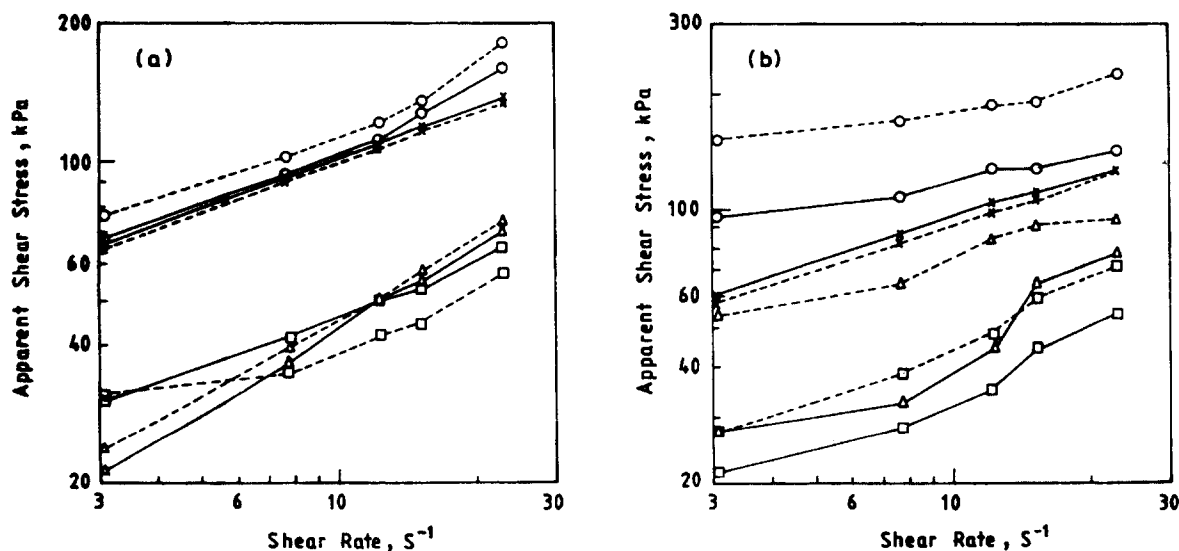
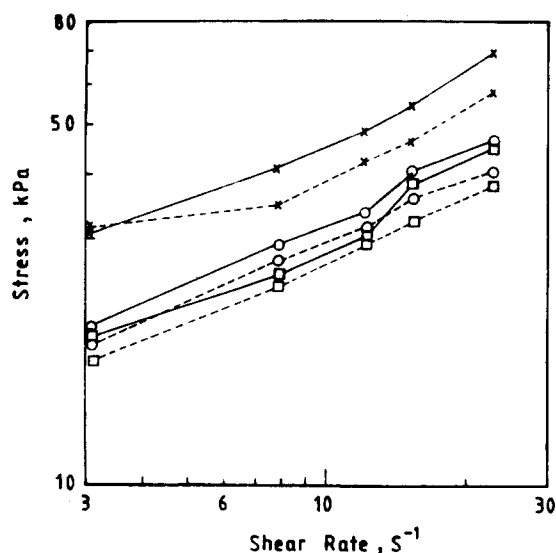


Figure 10 Apparent shear stress versus apparent shear rate plots of carbon black filled compounds showing the effect of blowing agent and curing agent at different temperatures and after 3 and 6 min of extrusion time: (a) 140°C; (b) 150°C; (—) 3 min; (---) 6 min; C<sub>1</sub> (×); C<sub>2</sub> (○); C<sub>3</sub> (□); C<sub>6</sub> (△)



**Figure 11** Plots of apparent shear stress versus shear rate with variation of blowing agent at different extrusion times in carbon black filled compounds in absence of curing agent at 140°C: (—) 3 min; (- - -) 6 min; C<sub>3</sub> (×); C<sub>4</sub> (○); C<sub>5</sub> (□)

of curing agent and blowing agent of carbon black filled compounds after 3 and 6 min extrusion at 140 and 150°C. Figure 10(a,b) show the gradual increase in the shear stress with the increase in the shear rate. The compound without the curing agent and the blowing agent follows the power law irrespective of temperature and extrusion time. The compounds containing either the blowing agent or curing agent or both show a non-linear relationship between shear stress and shear rate. The presence of only blowing agent in the compound restricts the stress rise with shear rate irrespective of the temperature and the extrusion time. The retardation in stress rise at high shear rate is due to the decomposed gas as a result of the decomposition of the blowing agent. However, in the presence of both the curing and the blowing agents, the decomposed gas is unable to release from the compound and restrict the increase in shear stress with shear rate. Compounds containing curing agent show an increase in stress compared to the gum compound

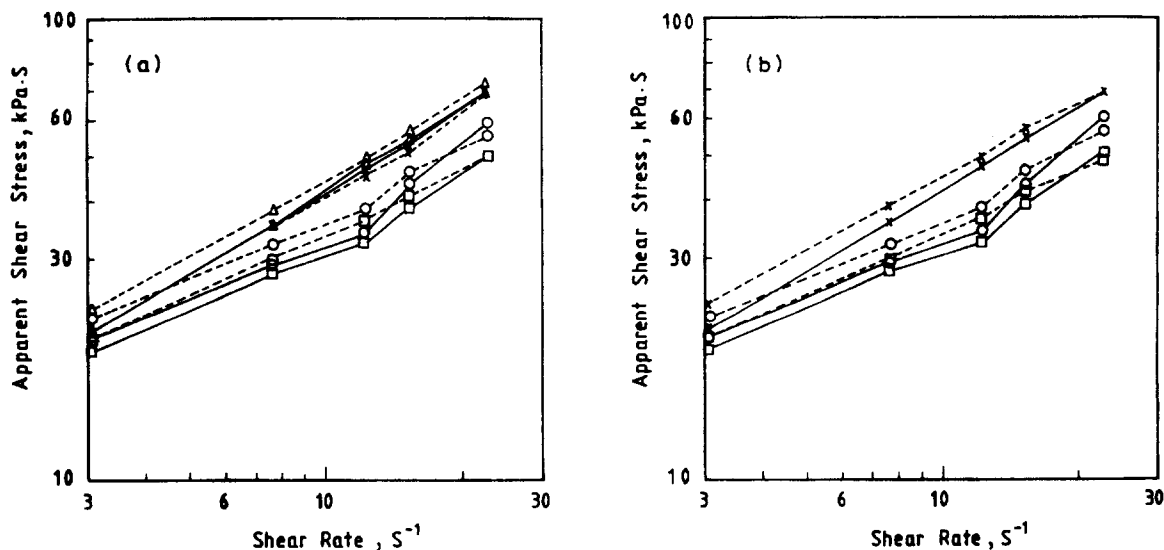
at higher extrusion time as curing takes place to some extent. Incorporation of blowing agent in addition to the curing agent decreases the stress considerably owing to encapsulation of decomposed gas. Similar curves were also obtained at 150°C after 3 and 6 min extrusion time (Figure 10(b)). The decrease in the stress with blowing agent in the system containing curing agent is more pronounced. The compound containing curing agent is partially cured and at the same time the blowing agent decomposes to produce gases. These gases dissolve or form microbubbles which are unable to escape from the system by diffusion and thereby reduces the stress.

*Effect of blowing agent loading in the absence of curing agent.* Figure 11 exhibits the plots of shear stress ( $\tau_{wa}$ ) versus shear rate with the variation of blowing agent loading at 140°C in carbon black filled system with different extrusion times. With the increase in blowing agent loading, the shear stress has a pronounced effect at higher shear rate than that at lower shear rate. At longer times the rate of rise in shear stress is restricted with the increase in blowing agent loading. Blowing agent decomposition is facilitated at longer time and also at higher shear rate. Hence, the rate of rise in shear stress is predominantly decreased at higher time and shear rate.

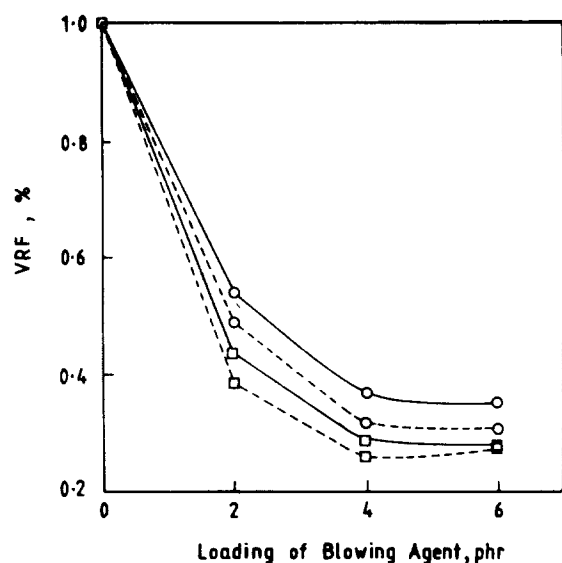
*Effect of blowing agent loading in presence of curing agent.* Figure 12 shows the plots of apparent shear stress ( $\tau_{wa}$ ) versus shear rate with different loading of blowing agent in the presence of curing agent in carbon black filled system at 140 and 150°C. The stress is found to decrease with increase in the blowing agent loading. After 6 min extrusion time the decrease in stress at higher shear rate is more than that at lower shear rate at both temperatures (Figure 12(b)). This may be due to the breakdown of blowing agent which is enhanced owing to higher shear rate, extrusion time and temperature.

*Viscosity reduction factor*

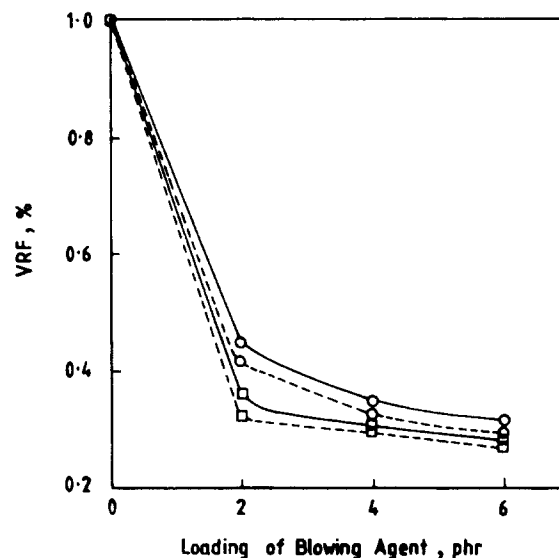
For practical interest a correlation between the extent of viscosity reduction and the loading of blowing agent is



**Figure 12** Plots of apparent shear stress versus shear rate with variation of blowing agent at different temperatures and extrusion times in carbon black filled compounds in presence of curing agent: (a) 140°C; (b) 150°C; (—) 3 min; (- - -) 6 min; C<sub>6</sub> (×); C<sub>7</sub> (○); C<sub>8</sub> (□)



**Figure 13** The viscosity reduction factor (VRF) at different shear rates in carbon black filled compounds with blowing agent loading at different extrusion times in absence of curing agent at 140°C: (—) 3 min; (---) 6 min; (○) 3.074 s<sup>-1</sup>; (□) 23.055 s<sup>-1</sup>



**Figure 14** The viscosity reduction factor (VRF) at different shear rates in carbon black filled compounds with blowing agent loading at different extrusion times in presence of curing agent at 140°C: (—) 3 min; (---) 6 min; (○) 3.074 s<sup>-1</sup>; (□) 23.055 s<sup>-1</sup>

made. The viscosity reduction factor (VRF) is defined by

$$\text{VRF} = \frac{\text{Viscosity of the mixture of the compounds and blowing agent}}{\text{Viscosity of the compounds}}$$

i.e.

$$\text{VRF} = \frac{\bar{\eta}(\dot{\gamma}, T)}{\eta(\dot{\gamma}, T)}$$

The VRF at different shear rates and for various combinations of curing agent and blowing agent are presented in Figures 13 and 14 for a fixed temperature. For a given blowing agent loading the VRF is found to be dependent on shear rate, extrusion time and temperature. Also VRF decreases with shear rate, extrusion time and temperature. VRF shows a decreasing trend with increase in blowing agent loading. The decrease in the VRF value is more in the presence of curing agent which is enhanced at higher temperature and extrusion time. The usefulness of Figures 13 and 14 is that one can predict the viscosities of the mixture of EPDM compound and blowing agent with information on the viscosities of virgin compound alone at the desired shear rate and temperature.

## CONCLUSIONS

- (1) From the morphological study it is observed that the pores in the extrudate are not spherical in nature. The number of cells in the extrudate increases with the increase in the shear rate, blowing agent loading and temperature.
- (2) The apparent shear stress increases with the increase in shear rate. The increase is non-linear in the presence of the curing agent and the blowing agent. The apparent shear stress value is found to decrease with the addition of the blowing agent for both gum and black filled compounds.

- (3) The die swell increases with shear rate in the presence of both the curing agent and the blowing agent compared to the values obtained for base compounds.
- (4) The viscosity reduction factor (VRF) decreases with the increase in shear rate, temperature and the blowing agent loading.

## ACKNOWLEDGEMENTS

We are grateful to the Council of Scientific and Industrial Research, Government of India, for providing financial support to carry out this work.

## REFERENCES

1. Bigg, D.M., Preston, J.R. and Banner, D., *Polym. Eng. Sci.*, 1976, **16**, 706.
2. Gonzalez, H., *J. Cell. Plast.*, 1976, **12**, 49–58.
3. Oyangi, Y. and White, J.L., *J. Appl. Polym. Sci.*, 1979, **23**, 1013–1026.
4. Han, C.D., Kim, Y.W. and Malhotra, K.D., *J. Appl. Polym. Sci.*, 1976, **20**, 1583.
5. Han, C.D. and Villamizar, C.A., *Polym. Eng. Sci.*, 1978, **18**, 687.
6. Ramesh, N.S., Rasmussen, D.H. and Campbell, G.A., *Polym. Eng. Sci.*, 1991, **31**, 1657.
7. Lee, S.-T., *Polym. Eng. Sci.*, 1993, **33**, 418.
8. Kraynik, A.M., *Polym. Eng. Sci.*, 1981, **21**, 80.
9. Denecour, R.L. and Gent, A.N., *J. Polym. Sci.*, 1968, **A6**, 1852.
10. Gent, A.N. and Tompkins, P.A., *J. Appl. Phys.*, 1969, **40**, 2520.
11. Stewart, C.W., *J. Polym. Sci. A2*, 1970, **8**, 937.
12. Dutta, A. and Cakmak, M., *Rubber Chem. Technol.*, 1992, **65**, 778.
13. Han, C.D., *Rheology in Polymer Processing*, Academic Press, New York, 1976.
14. Han, C.D. and Ma, C.-Y., *J. Appl. Polym. Sci.*, 1983, **28**, 831.
15. Han, C.D. and Ma, Chin-Yuan, *J. Appl. Polym. Sci.*, 1983, **28**, 851.