Rheological Behavior of Ethylene–Octene Copolymer Vulcanizates: Effect of Blowing Agent and Precipitated Silica Filler

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ABSTRACT: An experimental study of the rheological behavior of ethylene–octene copolymer vulcanizates in extrusion containing blowing agent has been carried out. The cell morphology development has been studied through a scanning electron microscope. Rheological properties of unfilled and precipitated silica-filled systems with variations of blowing agent, extrusion temperature, and shear rate have been studied by using a Monsanto processibility tester (MPT). The total extrusion pressure (P_T), apparent shear stress (τ_{wa}), apparent viscosity (η_a), and die swell (%) of the unfilled and silica-filled compounds have been determined by using MPT. The effect of blowing agent (ADC) on the rheological properties of the vulcanizates has also been investigated. There is a reduction of stress and viscosity with blowing agent loading. It was observed that the incorporation of a blowing agent led to decreased shear thinning behavior resulting in an increase in power law index. The viscosity reduction factor (VRF) of unfilled vulcanizates is found to be dependent on the concentration of the blowing agent, shear rate, and temperature, whereas VRF of silica-filled vulcanizates is found to be dependent on shear rate, temperature, and blowing agent concentration. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1132–1138, 2003

Key words: rheological properties; blowing agent; cell morphology; silica filler

INTRODUCTION

The rheological characterization of polymeric materials is one of the most important steps in the various problems encountered in polymer processing. Extrusion of polymeric materials containing a blowing agent is an important industrial processing operation.[1–2] In comparison to thermoplastics where extrusion foaming is a standard practice and where gas bubbles are generated by chemical and physical blowing agents within the thermoplastic melt extrusion, compounded elastomers containing chemical blowing agents are extruded at a lower temperature to shape the product and subsequently to heat treat to simultaneously bring about foaming and vulcanization.[3] However, under usual processing conditions, the physical and chemical blowing agents influence the rheological properties of the compounded elastomers.

Several authors[4–6] have investigated the 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. The mechanics of bubble growth in the polymer matrix is an important aspect of foam extrusion. Numerical and experimental studies of the bubble growth during the microcellular foaming process and the influence of temperature, saturation pressure, molecular weight, and nature of the physical blowing agent have been reported.[7] Effects of shear stress and pressure drop rate on thermoplastics foam has been reported.[8–10] The rheological aspect of thermoplastic foam extrusion was also described by a phenomenological model of the flow in an extrusion die.[11] Experimental studies of bubble growth in the elastomers are also found in the literature.[12–14] Bubble growth and physical properties of the thermoplastic elastomers have also been reported with respect to extrusion foaming.[3] The rheological properties of homopolymers in the molten state, polymer blends, and filled polymers were reported.[15] Hardly any literature is available that deals with the rheological properties of mixtures of molten polymer and blowing agents.[16–17] The effects of pressure drop rate on cell nucleation in a continuous process of microcellular polymers have been reported by Park et al.[18–19] The rheological properties of ethylene–propylene–diene rubber (EPDM) compounds have been studied with respect to the effects of blowing agent, curing agent, silica filler, and carbon black filler.[20–21] Recently, the rheology of molten polystyrene with dissolved supercritical and near-critical gases has been reported by Kwag et al.[22]

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TABLE I
Formulations of Unfilled and Filled Vulcanizates[a]

	Mix no.							
	G_0	G_2	G_4	G_6	ES_1	ES_2	ES_3	ES_4
Engage-8150	100	100	100	100	100	100	100	100
Silica	0	0	0	0	30	30	30	30
Paraffin oil	2	2	2	2	9	9	9	9
DEG	—	—	—	—	2	2	2	2
ADC-21	0	2	4	6	0	2	4	6

[a] Each mix contains ZnO, 3; stearic acid, 1; and dicumyl peroxide(DCP 98%), 1.2 pphr.

It may be summarized that, in controlling the formation and growth of gas bubbles in a viscous molten polymer, several factors are involved: the type of blowing agent (physical or chemical), the concentration of blowing agent, melt extrusion temperature, melt viscosity, and elasticity of polymer, pressure profiles in the extruder and in the extrusion die, solubility of the gas in the polymer, and its diffusivity in the polymer. In the present study, the rheological behavior of unfilled and precipitated silica-filled ethylene–octene copolymer vulcanizates with variation of blowing agent loading were reported. The effect of temperature in extrusion has also been investigated. The morphological studies of the extrudate were investigated by using scanning electron microscopy (SEM) to characterize the cellular structure of the extrudates.

EXPERIMENTAL

Materials

Engage–8150 (ethylene–octene copolymer) containing 25 wt % octene monomer with a melt flow index of 0.5 g/10 min (190°C/2.16 kg), a density of 0.868 g/mL, and a Mooney viscosity, ML_{1+4} (121°C) of 35, manufactured by DuPont Dow Elastomer Co. has been used. The filler used was precipitate silica, manufactured by Degussa AG, Huerth, Germany, having a specific gravity of 2; Brunauer, Emmett, and Teller (BET) surface area, 160–120 m^2/g; and particle size, 10–20 nm. The dicumyl peroxide (DCP) used was of 98% purity, manufactured by Aldrich Chemical Co., USA. Azodicarbonamide (ADC), the blowing agent, was ADC-21, manufactured by High Polymer Lab, New Delhi, India. The diethylene glycol (DEG) had a density of 1.115 g/mL and was manufactured by E. Merck, Mumbai, India.

Compounding and sample preparation

Engage was compounded with the ingredients according to the formulations of the mixes (Table I). Compounding was done in a Brabender Plasticoder (model PLE 330) having cam-type rotors. The copolymer was first melted at 80°C with a rotor speed of 60 rpm for 2 min, after which other ingredients were added. With subsequent incorporation of filler, mixing was continued for another 3 min to ensure homogeneous distribution of ingredients. In the case of filled compounds, blowing agent was added along with the filler for good dispersion. Finally, curative was added. The hot mix was taken out and passed through the tight nip of a two-roll mill maintained at room temperature, to form a sheet in one pass of the roll.

Measurement of rheological properties

Rheological properties of the samples have been studied with a Monsanto processibility tester (MPT, No. 83077) at temperatures of 100, 110, and 120°C. The capillary had a 2 mm diameter with a length-to-diameter ratio (L/D) equal to 16 : 1. The test samples were charged into the barrel and preheated for 3 min for uniform temperature distribution and were extruded with different piston rates of 0.05, 0.1, 0.25, and 0.5 in./min^{-1} with time. The piston rates correspond to the apparent shear rates (γ_{wa}) of 7.685, 15.37, 38,425, and 76.85 s^{-1}, respectively. The apparent wall shear rate γ_{wa} and apparent wall shear stresses τ_{wa} are calculated from the 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 τ_{wa} is the shear stress at the wall, d is the capillary diameter, l is the capillary length, ΔP is the pressure drop over the capillary length, measured with a pressure gauge at the inlet of capillary, $\dot{\gamma}_{wa}$ is the apparent rate of shear at the wall, and 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 (die swell at the exit of the die as soon as the extrudate comes out) data were directly recorded with a built-in laser scanning system.

SEM

SEM photomicrographs of razor-cut surfaces of the microcellular extrudates were obtained by using a JEOL JSM 5800 scanning electron microscope. The
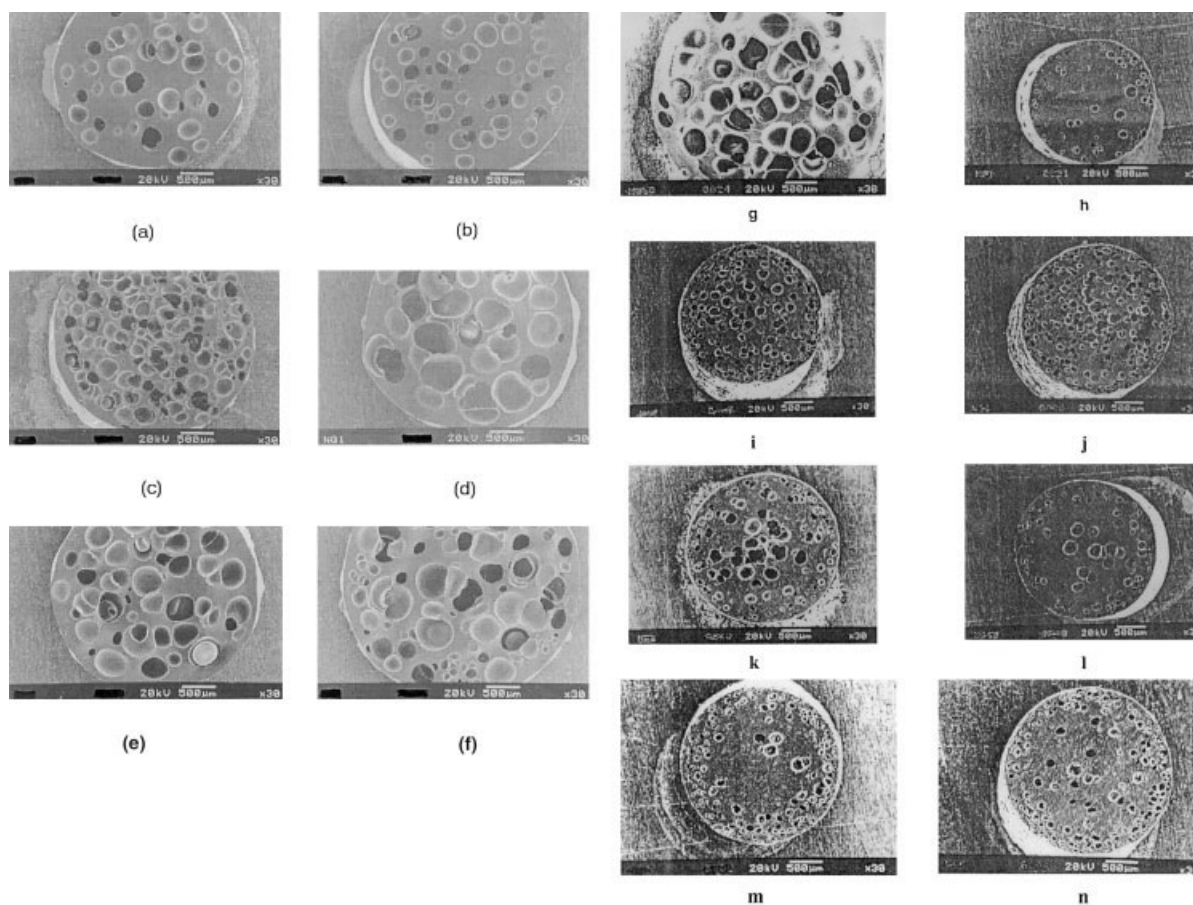
Figure 1 SEM photomicrographs of unfilled and precipitated silica-filled extrudates at 30× magnification: (a) G_2, 7.685 s^{-1}, 100°C; (b) G_4, 7.685 s^{-1}, 100°C; (c) G_6, 7.685 s^{-1}, 100°C; (d) G_2, 7.685 s^{-1}, 120°C; (e) G_2, 15.37 s^{-1}, 100°C; (f) G_2, 38.425 s^{-1}, 100°C; (g) G_2, 76.85 s^{-1}, 100°C; (h) ES_2, 7.685 s^{-1}, 100°C; (i) ES_3, 7.685 s^{-1}, 100°C; (j) ES_4, 7.685 s^{-1}, 100°C; (k) ES_2, 7.685 s^{-1}, 120°C; (l) ES_2, 15.37 s^{-1}, 100°C; (m) ES_2, 38.425 s^{-1}, 100°C; (n) ES_2, 76.85 s^{-1}, 100°C.

samples were gold coated by using a vacuum gold sputter machine for the SEM studies.

RESULTS AND DISCUSSION

Morphology of unfilled and silica-filled extrudates

SEM photomicrographs of the cross sections of the extrudates are shown in Figure 1. Quantitative image analysis[23] was used to analyze the photomicrographs to determine the average cell size or diameter. They illustrate the effects of blowing agent, shear rate, and temperature on the cell sizes of the extrudates. The formation of the gas bubbles that occur inside the capillary depends on the pressure, temperature, and concentration of the blowing agent. The average cell sizes of the extrudates with variation of blowing agent, temperature, and shear rates are summarized in Table II. In the case of both unfilled [Fig. 1(a, b, c)] and silica-filled vulcanizates [Fig. 1(h, i, j)], the number of cells increases with increasing blowing agent concentration. With an increase in the concentration of blowing agent, the free volume of the system is increased;

thereby, the melt viscosity is decreased [24] and its degree of supersaturation increased after leaving the die,[25] resulting in a higher nucleation rate. However,

TABLE II
The Average Cell Size of the Extrudate with Variation of Blowing Agent, Temperature, and Shear Rate

Mix no.	Shear rate (s^{-1})	Temperature (°C)	Average cell size (μm)
G_2	7.685	100	206
G_4	7.685	100	200
G_6	7.685	100	195
G_2	7.685	120	410
G_2	15.37	100	222
G_2	38.425	100	348
G_2	76.85	100	360
ES_2	7.685	100	52
ES_3	7.685	100	43
ES_4	7.685	100	40
ES_2	7.685	120	90
ES_2	15.37	100	50
ES_2	38.425	100	45
ES_2	76.85	100	40
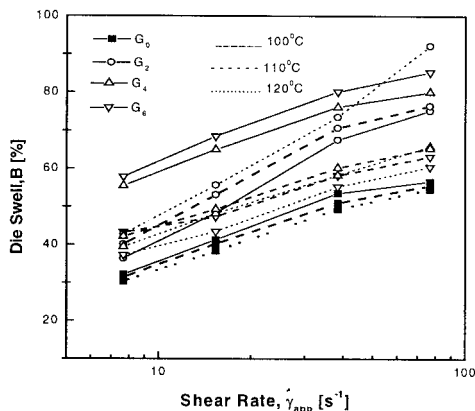
Figure 2 Die swell (%) versus shear rate plots of unfilled vulcanizates at different temperatures.
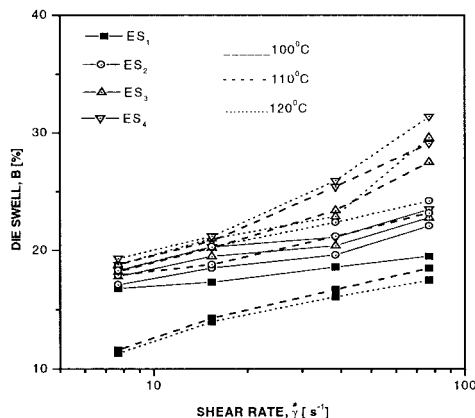

Figure 3 Die swell (%) versus shear rate plots of silica-filled vulcanizates at different temperatures.

the cell sizes at a lower concentration of blowing agent are smaller than the cell sizes at the higher concentration of blowing agent. At a lower concentration of blowing agent, the number of nucleation sites are less, and hence, the total void volume is less, resulting in an increase in absolute melt viscosities. This effectively leads to a suppression of bubble growth and hence a reduction in cell size. On the other hand, at a higher concentration of blowing agent, there is a decrease in melt viscosities, resulting in increased bubble growth and cell sizes.[26] With an increase in temperature, the cell sizes as well as number of cells increases in the case of unfilled [Fig. 1(a, d)] as well as in the case of silica-filled [Fig. 1(h, k)] vulcanizates. This is due to the fact that an increase in temperature lowers the melt viscosity, resulting in a faster nucleation rate, which allows an increase in the growth of the bubbles and hence an increase in cell sizes. Figure 1 demonstrates that in the case of unfilled [Fig. 1(a, e, f, g)] vulcanizates, with increase in shear rate, the number of cells as well as cell sizes increase. This is due to the fact that shear rate promotes nucleation.[8] In the case of silica-filled [Fig. 1(h, l, m, n)] vulcanizates, it is observed that with an increase in shear rate, the number of cells increases but the average cell sizes decreases.

Die swell

Effect of blowing agent in unfilled and silica-filled vulcanizates at different temperatures

The die swell of the unfilled vulcanizates at 100, 110, and 120°C are shown in Figure 2. It is evident that the die swell of the unfilled vulcanizates without blowing agent increases with increasing shear rate and decreasing temperature. In the case of unfilled vulcanizates, at 100°C, die swell increases with an increase in shear rate and blowing agent concentration. With the addition of 2 phr blowing agent, the die swell increases with shear rate and temperature. With further addition of blowing

agent, the die swell increases with shear rate but shows a decreasing trend at higher temperatures. This may be due to the fact that at higher temperature and at high blowing agent concentration the rate of nucleation is higher, which leads to a breakdown of the cells and release of decomposed gas from the cells and therefore, die swell decreases. Though with increase in blowing agent and temperature, there is increase in rate of nucleation (i.e., increase in void volume), the decrease in die swell at a higher temperature may be attributed to collapse of the cells. Figure 3 shows the die-swell values of the silica-filled vulcanizates with shear rate. It is evident that die swell of the vulcanizate without blowing agent increases with increasing shear rate and decreasing temperature. With blowing agent loading, die swell increases with increasing shear rate and temperatures. However, for a particular blowing agent loading, the relative increase in die swell in filled vulcanizates are less than those of unfilled vulcanizates. This can be attributed to the presence of filler, although the presence of filler helps in the nucleation of the cell but increases the
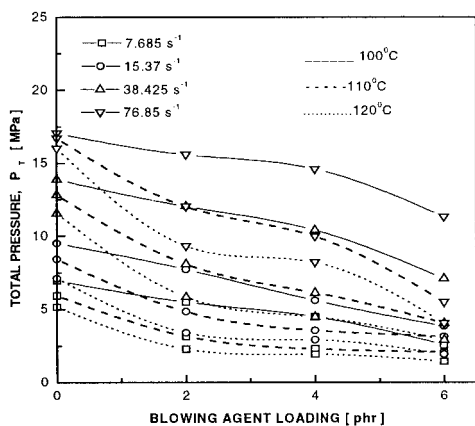
Figure 4 Total extrusion pressure (P_T) of unfilled vulcanizates as a function of blowing agent loading at various shear rates and at different temperatures.
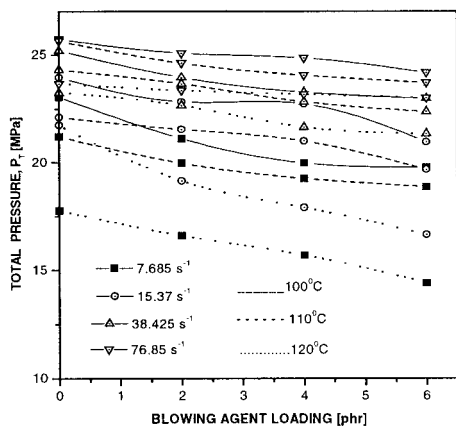
Figure 5 Total extrusion pressure (P_T) of silica-filled vulcanizates as a function of blowing agent loading at various shear rates and at different temperatures.

Figure 7 Plots of apparent shear stress versus apparent shear rate of silica-filled vulcanizates at different temperatures.

melt viscosity of the vulcanizates and restricts the growth of the cells, resulting in decrease in die swell in comparison to the unfilled vulcanizates.
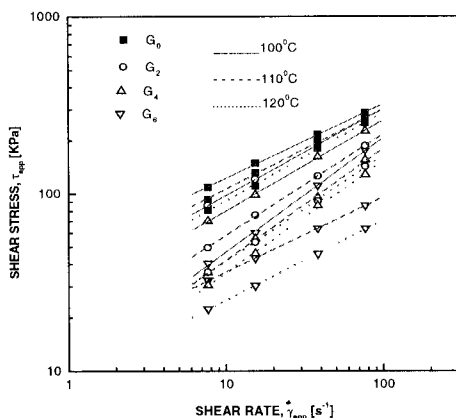
Total extrusion pressure

The total extrusion pressure drop (P_T) of unfilled and silica-filled vulcanizates are plotted as a function of the concentration of blowing agent loading in Figures 4 and 5, respectively. It is seen that P_T decreases with an increase of blowing agent loading at any shear rate. Initially the decrease is slow (at 2 phr) but with an increase in blowing agent loading, the decrease is sharper in the case of filled vulcanizates than in the unfilled vulcanizates. With an increase in shear rate, P_T increases for unfilled as well as filled vulcanizates.
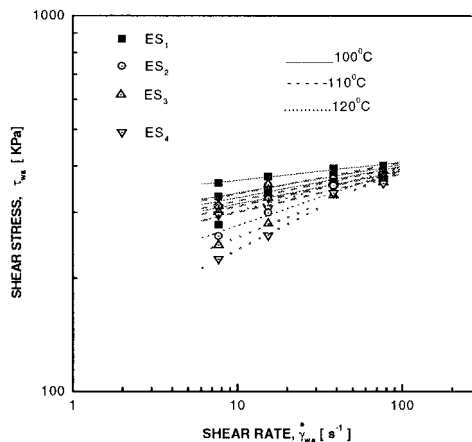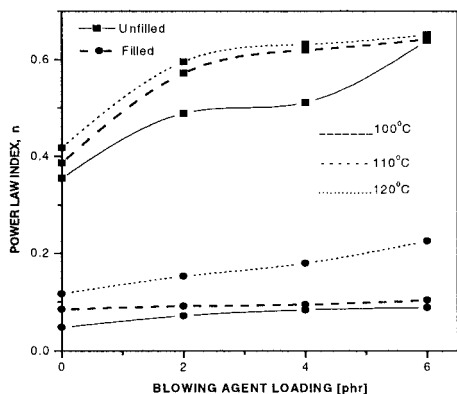
Stress behavior

Effect of blowing agent and temperature

Figures 6 and 7 show the bilogarithmic plots of shear

stress (τ_{wa}) against rate ($\dot{\gamma}_{wa}$) of unfilled and silica-filled vulcanizates, respectively. It is evident that with an increase in shear rate, there is an increase in shear stress for both unfilled as well as filled vulcanizates and is approximately linear in nature. Thus, the power law equation was applied to express the rheological behavior of the system, for instance,

$$\tau = k(\dot{\gamma}_{wa})^n \tag{4}$$

where n is the Power law index (pseudoplasticity index) and k is the consistency index [i.e., the viscosity (Pa s^n) at unit shear rate]. The linear regression analysis was applied to obtain the slope n and intercept k. The values of n and k are summarized in Table III. Figure 8 shows the plots of power law index against blowing agent loading at three different temperatures. It is interesting to note that there is an increase in power law index value with an increase in blowing agent concentration for unfilled as well as silica-filled vulcanizates. For any particular vulcanizate, there is also an increase in power law index value for an increase in temperature. The increase in power law index value observed may be explained in terms of the

Figure 6 Plots of apparent shear stress versus apparent shear rate of unfilled vulcanizates at different temperatures.

TABLE III
Power Law Constants. $K \times 10^3$ Pa s^n

| Mixes | 100°C | | 110°C | | 120°C | |
	n	k	n	k	n	k
G_0	0.355	1.83	0.387	1.752	0.418	1.664
G_2	0.489	1.499	0.572	1.19	0.596	1.02
G_4	0.512	1.39	0.63	0.99	0.632	0.94
G_6	0.64	1.02	0.642	0.94	0.652	0.92
ES_1	0.431	2.005	0.454	1.931	0.552	1.783
ES_2	0.447	1.936	0.462	1.897	0.55	1.696
ES_3	0.452	1.888	0.464	1.868	0.571	1.64
ES_4	0.459	1.87	0.468	1.834	0.602	1.568

Figure 8 Effect of blowing agent concentration on power law index at different temperatures.

Figure 10 Plots of apparent viscosity versus apparent shear rate of silica-filled vulcanizates at different temperatures.
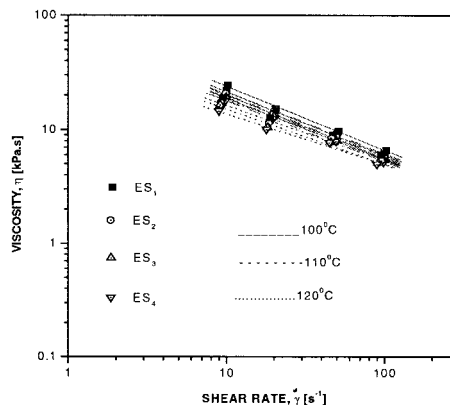
temperature and free-volume effects on viscosity. It is well known that the power law index increases with a rise of temperature for all polymers.[27] However; a temperature increase means an increase in free volume of the polymer. A free volume increase, which reduces the glass transition temperature, can also be achieved by the dissolution of a gas into a polymer.[28–31] Therefore, the increase in temperature and dissolution of a gas into a polymer have an equivalent effect on viscosity and shear thinning behavior, which explains the result. It is also observed that the apparent shear stress decreases, as the concentration of blowing agent is increased.

Viscosity behavior

Figures 9 and 10 show the plots of viscosity versus shear rate at 100, 110, and 120°C of unfilled and filled vulcanizates, respectively. All viscosity data in Figures 9 and 10 are Rabinowitch-corrected[32] values. A reduction in the viscosity was observed for the vulcanizates with blowing agent compared to the vulcanizates without blowing agent. With an increase in blowing

agent concentration and temperature, the viscosity tends to decrease.

VRF

It is of practical interest to obtain correlation between the extent of viscosity reduction and the concentration of blowing agent loading. The viscosity reduction factor is defined as

$$VRF = \frac{\text{Viscosity of the compounds and the blowing agent}}{\text{Viscosity of the compound}} \quad (5)$$

$$VRF = \frac{\eta\,(\dot{\gamma},T)_{CBA}}{\eta\,(\dot{\gamma},T)_{C}} \quad (6)$$

By using viscosity data, the VRF at different shear rates and melt temperatures have been calculated for both unfilled and silica-filled vulcanizates. The plots of VRF versus blowing agent loading for unfilled and filled vulcanizates are shown in Figures 11 and 12, respectively. In

Figure 9 Plots of apparent viscosity versus apparent shear rate of unfilled vulcanizates at different temperatures.
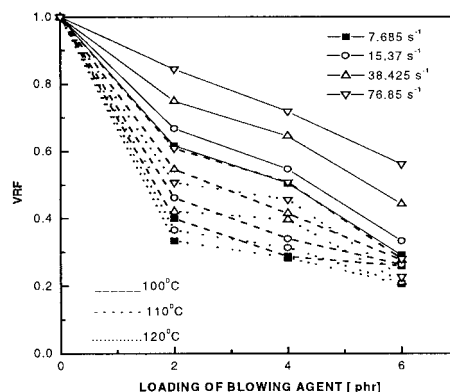
Figure 11 Plots of viscosity reduction factor of unfilled vulcanizates as a function of blowing agent loading at different shear rates.
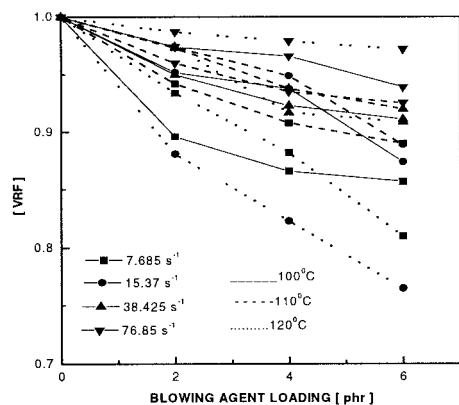
Figure 12 Plots of viscosity reduction factor of silica-filled vulcanizates as a function of blowing agent loading at different shear rates.

the case of unfilled vulcanizates, the VRF decreases as the blowing agent concentration is increased. VRF is found to be shear rated and temperature dependent. For a particular concentration of blowing agent loading, VRF increases with an increase in shear rate and decreases with an increase in temperature. In the case of silica-filled vulcanizates, the VRF decreases with an increase in blowing agent loading at any shear rate and temperature. However, VRF does not display systematic dependence on shear rate and temperature.

CONCLUSIONS

1. The photomicrographs of the extrudates reveal that the cells are spherical in nature. The number of cells in the extrudate increases with an increase in blowing agent loading, temperature, and shear rate in the case of both unfilled and silica-filled vulcanizates.

2. Die swell increases with shear rate for vulcanizates with and without blowing agent. However, for a particular blowing agent loading, the relative increase in die swell in silica-filled vulcanizates are less than those of unfilled vulcanizates.

3. The total extrusion pressure drop (P_T) decreases with an increase in blowing agent concentrations but for a particular blowing agent concentration, the P_T increases with an increase in shear rate.

4. The apparent shear stress increases approximately linearly with the increase in the shear rate. A considerable reduction in viscosity was observed with an increase in blowing agent concentration and temperature.

5. The power law index was found to increase with increase in blowing agent concentration.

6. For unfilled vulcanizates, the VRF decreases with an increase in blowing agent concentration but increases with an increase in shear rate and decreasing temperature. In the case of silica-filled vulcanizates, VRF decreases with an increase in blowing agent loading. However, for a particular blowing agent concentration, VRF is found to be dependent on shear rate and temperature.

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