Deformation of poly (dienes) below T_g

Part 1 *Radical formation and crazing in cross-linked poly(dienes)*

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Cross-linked poly (dienes) (polychloroprene, polyisoprene and polybutadiene) are shown to exhibit crazing when subjected to low strain-rate tensile tests at low temperatures. Conditions for crazing to occur in the polybutadienes are examined. It is found that observable crazing occurs providing the rubbers are (a) slightly oriented, (b) stretched below their glass transition temperature (T_g) and (c) deformed in an environment which is close to its liquefaction or sublimation point. Gases evolved after low temperature testing are shown to be dissolved gases from the test environment. The interrelationship between the mechanical properties of the rubbers, quantity of gas absorbed and the radicals formed by scission of the network molecules is explored.

1. Introduction

Crazing of thermoplastics has been extensively researched and much of the work in this area has been reviewed by Kambour [1]. The majority of the work is concerned with crazing in glassy thermoplastics at, or near, room temperature, when the polymer is in contact with a liquid crazing agent, such as an alcohol [2]. It was reported by Parrish and Brown [3] that liquid nitrogen and other cryogenic liquids, with the exception of helium, were also crazing agents for some glassy thermoplastics. The effect of nitrogen, near its liquefaction temperature, as a crazing agent on cross-linked natural rubber during tensile testing, had been previously observed by Andrews and Reed [4]. However, the effect was not then recognized as crazing, since the specimens could only be observed after they had been warmed above their glass transition temperature (T_g) and hence to the rubber condition. This resulted in the absorbed gas expanding, causing the specimen to become foamed. In this condition, the individual craze striations were not distinguishable. The gas giving rise to the foaming (crazing) was unfortunately incorrectly identified at that stage

and subsequently correctly diagnosed as absorbed environmental gases.

Low temperature crazing of polymers in cryogenic liquids and carbon dioxide has been observed in isotactic polypropylene [5, 6], polychloroprene [7], polycarbonate [8], and poly(methylmethacrylate) [9]. It has been established that nitrogen, argon, oxygen and carbon dioxide all act as crazing agents over a limited temperature range, which extends from the liquefaction temperature to approximately 50 K above the liquefaction temperature. At equivalent temperatures in either a vacuum or helium, the thermoplastics break in a brittle manner when tensile-tested [8]. Introduction of the crazing agent gases results in crazing, with a consequent lowering of the yield stress below that of the brittle fracture strength at equivalent temperatures. Brown has established [8] that the yield stress for crazing increases with reduction of the partial pressure of the gas until brittle fracture is observed. This is referred to by Brown as an intrinsic strength. Empirical relationships between the partial pressure of the gas, test temperature, yield and intrinsic stress have been determined by Imai and Brown [8, 9]. However,

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a fundamental understanding of the mechanism of low temperature crazing awaits development.

The present paper is concerned with the low temperature crazing of cross-linked poly(dienes) during tensile testing below their T_g. The objective is to assess the role and influence of nitrogen, argon, air, helium, sulphur dioxide and carbon dioxide on the mechanical behaviour of the poly(dienes) near the liquefaction temperatures of these gases. Additional information is available from complementary tests on the radical formation accompanying crazing in the poly(dienes), as measured by electron spin resonance (ESR).

It has been previously reported that considerable quantities of nitrogen gas or liquid are absorbed by natural rubber and polybutadiene during tensile testing at temperatures below 150 K [4, 10, 11]. This gas can be subsequently released from the sample by warming it to room temperature, causing the absorbed gas/liquid to expand and the sample to become a foam. A range of different mechanical behaviour is obtained in the rubbers when they are tested below their T_g. The behaviour may be brittle, ductile by macroscopic shear yielding without obvious crazing, crazing involving the absorption of large quantities of environmental gases, or apparently homogeneous drawing of the sample without crazing. The mode of deformation obtained depends on the test strain-rate, degree of cooling below T_g, test environment and the degree of orientation in the sample at the commencement of the tensile test. The latter orientation is effected above the T_g of the material, when it is in the rubber-like condition, by extension of the specimen at room temperature and subsequently quenching it to the test temperature in the extended condition. It has been shown that crazing is confined to samples which are pre-oriented (50 to 400%), tested at low strain-rates (less than $10^{-1} \sec^{-1}$) and tested at a temperature close to the liquefaction temperature of the environment [11].

This paper extends these results to consider other poly(dienes) tensile tested in various environments so that the condition for environmental controlled crazing and the maximum influence of the environment on the mechanical properties may be characterized and the mechanism of the penetration of the environment into the polymer deduced. A study is made of both the quantity and composition of the evolved gases from the low temperature tested polybutadiene. Concomitant with the deformation of the samples and the craze formation is the accumulation of the quantity of radicals produced. The interrelationship between the quantity of radicals formed, crazing and the mechanical properties is considered.

2. Experimental details

The poly(dienes) used were cross-linked using dicumyl peroxide (Hercules Powder Co) for the polybutadiene (Cariflex BR 1202 – Shell Ltd) and polyisoprene (cis 1,4 96% cis – Shell Ltd), while zinc oxide was used to cross-link the polychloroprene (Neoprene W, DuPont Ltd). Sheets of rubbers were prepared by hot-pressing the previously milled rubbers to which the cross-linking agent had been added. Dumb-bell specimens were then stamped from the 2 mm thick sheets, mounted in suitable clamps and then pre-oriented by the required amount at room temperature. Maintaining the pre-orientation, the specimens were then placed either directly into liquid nitrogen or mounted in a specially designed cabinet for low temperature tensile testing [12]. The environment within the cabinet could be changed by passing gas through it from a gas cylinder, while the temperature was controlled down to liquid nitrogen temperature by passing liquid nitrogen through an outer cooling jacket. The cabinet was attached to an Instron universal testing machine, so that tensile tests could be effected in the normal manner.

Since the deformation characteristics of the specimens could not be observed in the cabinet, additional tests were performed in a different chamber. Details of this apparatus are published separately [13]. The apparatus consisted of a straining frame mounted inside a double walled vacuum flask. Both the environment and temperature within the flask could be controlled in a similar manner to that of the Instron cabinet. While the majority of the flask walls were silvered, two panels were left clear in order that the specimen could be observed and photographed at the low temperatures.

After tensile testing, a representative sample of the specimens were taken and the gases evolved from them studied by mass spectroscopy, as they were warmed to room temperature. The glassware used for these tests is shown in Fig. 1 which is basically a tube divided into two by a glass seal. The mechanically deformed specimens were placed in chamber A by passing them along tube B, before the tube was evacuated and then sealed. The whole
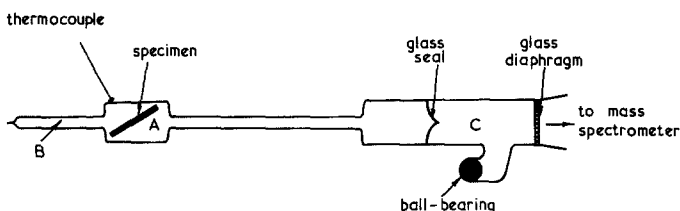
Figure 1 Glassware used for the analysis of absorbed gases by mass spectrometer.

operation was completed maintaining the specimen at or near 77 K. Although it is recognized that some gas will be lost from the sample during evacuation, this is mainly from the surface and the majority of the gas absorbed remained in the sample. While maintaining the sample at 77 K, by immersing the sample holder in liquid nitrogen, the mouth of the sample holder was then connected to a mass spectrometer. The larger bulb of the glassware (C) contained two items, a glass seal and a porous diaphragm. Once connected to the mass spectrometer, the region above the glass seal was evacuated and the glass seal then broken by dropping the ball-bearing onto it. The glass diaphragm prevented glass fragments passing into the mass spectrometer.

A background scan of the mass spectrometer was taken before the seal was broken. Then scans of the gases released from the sample were taken at 10 K intervals, as the specimen was warmed from 83 K to room temperature.

Finally, in addition to the tensile tests and the gas composition analysis, further specimens were tensile-tested at the low temperatures and then taken to a Varian E-9 ESR spectrometer. Measurements were made of the radical concentration resulting from the tensile test which could be correlated with the mechanical and gas analysis data. A full analysis of the ESR investigations has been described elsewhere [11, 14].

3. Modes of deformation

Three types of mechanical behaviour are observed for polybutadiene, polyisoprene and polychloroprene (with or without chemical cross-linking) stretched in nitrogen gas at 83 K. The modes are dependent on the degree of pre-test orientation, test strain-rate and cross-link density. They are typified by the stress—strain curves shown in Fig. 2. Type 1 curve indicates the stress—strain curve obtained when brittle behaviour occurs. In such cases the slope of the nominal stress—strain curve is always positive and no maximum in the load—deflection curve is observed. The other two modes of mechanical behaviour are ductile modes which appear to require some pre-orientation, since ductile behaviour is not observed in unoriented specimens at 83 K regardless of strain-rate. Intermediate pre-extension (100 to 300%) gives rise to a stress—strain curve of type 2 behaviour. A gradual load drop follows the upper yield point. Subsequent deformation produces a constant load
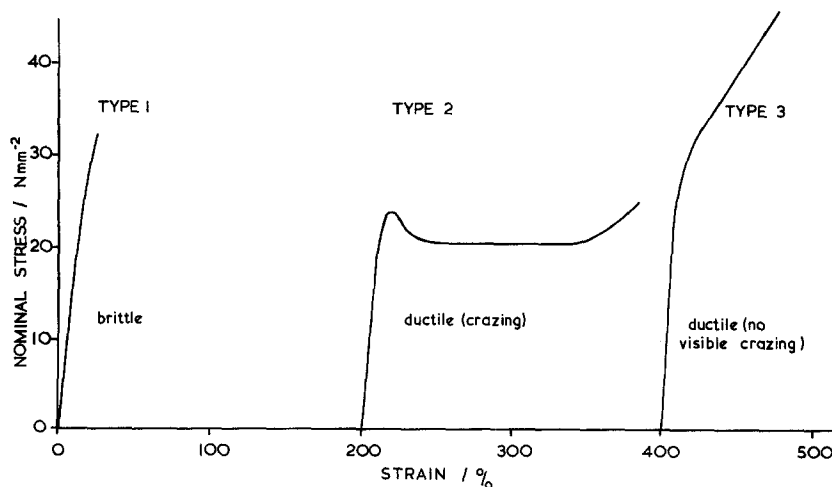

Figure 2 Different forms of stress—strain curves obtained with *cis*-polybutadiene at 83 K in a nitrogen environment. Intercept on the strain axis indicates pre-orientation of specimens applied at room temperature. Strain-rate $\simeq 10^{-3}$ sec^{-1}.
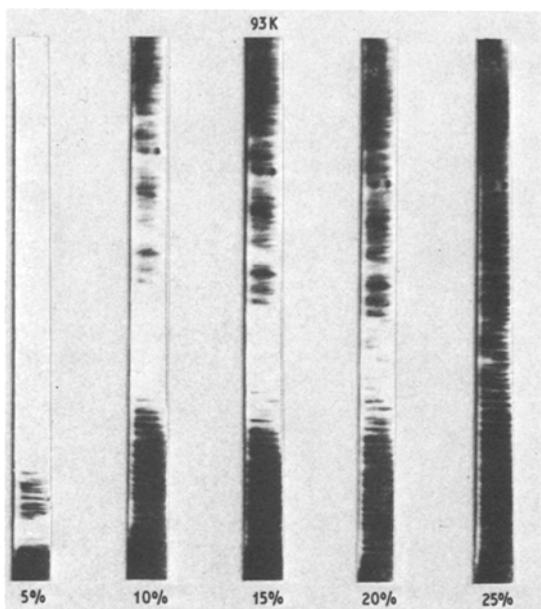
Figure 3 Development of deformation bands in poly-butadiene with increasing strain at 93 K in a nitrogen atmosphere.

curve changing to a slight increase in load near the fracture strain. Such specimens when warmed to room temperature are observed to have swollen bands and contain large quantities of gas.

For the type 2 mode of deformation, these narrow bands are first formed in the specimens at a stress level approximately $\frac{2}{3}$ that of the yield stress. They are approximately 0.5 mm thick and apparently randomly distributed over the length of the specimen as shown in Fig. 3.

Proliferation of these bands occurs as extension continues beyond the yield point. The bands are planar and normal to the specimen tensile axis. At, and subsequent to the yield point, these bands thicken, proliferate and adjacent bands coalesce. At the lowest temperature of testing (83 K) the bands traverse the specimen, apparently initiating from all four faces of the specimen. The bands initiate discretely, over the specimen length, prior to the yield point. After the yield point the bands thicken and interact with each other to form a broad localized region, as can be seen from the sequence in Fig. 3. Further extension results in the region gradually extending to incorporate more individual bands, until the whole specimen is consumed. Band growth occurs at the boundaries of the growing region and does not produce a localized change in the cross-sectional area of the specimen.

Since the bands are normal to the specimen axis and hence normal to the major principal stress and they are load bearing when they have traversed the specimen, it is considered that the bands are crazes. Hence the ductile mode associated with type 2 curves in Fig. 2 is associated with crazing [15–17].

Individual craze bands are no longer distinguishable in the poly(dienes) tested by the time macroscopic fracture occurs and the specimen is then essentially uniformly voided.

When the pre-test orientation exceeds approximately 400%, a third type of behaviour is observed (Type 3). The load–deformation curve shows (Fig. 2) no load maximum, no local band formation, no apparent penetration of gas into the polymer, and hence no apparent crazing. The pre-test orientation required to obtain type 3 behaviour is greater than the total strain at the termination of the constant load portion of type 2 curves and the type 3 curves tend to follow the rise in stress observed at the termination of the type 2 behaviour. Application of Considére's construction to true stress–strain curves following from type 2 curves indicate that the maximum load point is associated with the onset of plastic instability while the rise in load at the termination of the constant load portion of the curve indicates the end of plastic instability. Hence it appears that the large pre-orientation applied to specimens which subsequently exhibit type 3 behaviour serves to condition the material beyond the point where plastic instability can occur.

The magnitude of the load drop at yield when type 2 behaviour occurs decreases with increase in pre-orientation [18], approaching zero with the onset of type 3 behaviour. Hence the magnitude of the load drops and associated maximum loads at onset of yield with type 2 behaviour increase as the pre-orientation decreases and as the transition to brittle behaviour is approached.

In some instances, with specimens which receive no pre-test orientation, a maximum is observed on the load–extension curve just prior to fracture, indicating the onset of plastic instability. Such specimens exhibit a white band around the fracture surface, which is transverse to the loading axis. Such behaviour may be associated with initial craze formation which, because of the higher initial yield stress for craze yielding in lightly pre-oriented specimens, leads to catastrophic crack propagation. It is also possible that the increasing load drop

with decreasing pre-orientation leads to a greater energy release rate which leads to fracture rather than craze yielding. The craze yielding exhibited in type 2 behaviour is similar to that observed by Hoare and Hull in polystyrene [22]. Hoare and Hull state that the sudden yield drop is associated with a change in stain-rate, which may be a further factor in the transition from ductile to brittle behaviour.

4. Environmental control of the mechanical behaviour

The type 2 mode of ductile deformation was observed initially near the liquefaction temperature of nitrogen in a predominantly nitrogen atmosphere. Studies of whether the above-quoted conditions were the sole ones to give crazing in the poly(dienes) were made by varying the environment in which the tensile test was conducted.

Fig. 4 shows stress–strain curves for identically prepared and tested polybutadiene specimens, but tested in different environments. The curves clearly illustrate that the environment significantly influences the mechanical behaviour of the deformed specimens. Several important points are noteworthy.

(a) Using argon or air as the environment, crazing is still observed at 83 K for lightly oriented polybutadiene specimens. The liquefaction temperatures of these gases are not greatly different from that of nitrogen.

(b) In a helium atmosphere, a brittle behaviour results and no localized deformation bands are observed. The stress at fracture was greater than that observed for a similar specimen stretched in liquid nitrogen. The initial tangent modulus of polybutadiene in helium is 5 to 10% greater than in nitrogen under identical test conditions and approaches that for a highly oriented polybutadiene specimen.

(c) In a sulphur dioxide environment, a ductile mode of deformation was found, although gas absorption and crazing was not observed after the tensile test.

The crazing mode of ductility is clearly environmental controlled. Changing from nitrogen to helium during the tensile test at 83 K causes the ductile behaviour in nitrogen to convert to brittle behaviour in helium within 2 min of introducing the helium. The lapse of two minutes may indicate a rate-dependent process relating the environment to the mode of "diffusion" and "absorption" processes.

One difference between the two environmental gases used, helium and nitrogen, is their liquefaction temperatures. The liquefaction temperature for nitrogen is 77 K, close to the test temperature used; that for helium is $\simeq 4.2$ K. This suggests that crazing may only occur at or near the liquefaction temperature of the environment, a factor which has also been considered by Imai and Brown [9]. They suggested that the sole criterion for crazing was that the gas or liquid could be absorbed by the polymer. Polybutadiene specimens were, therefore, stretched in gaseous carbon dioxide at its sublimation temperature ($\simeq 195$ K) at atmospheric
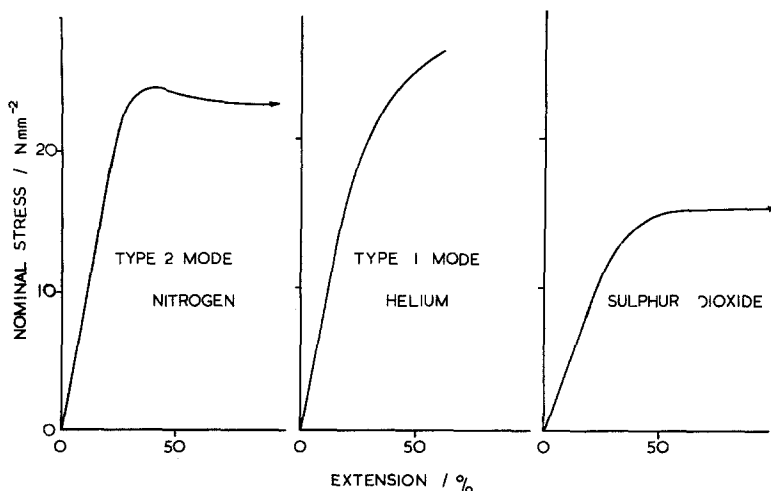

Figure 4 Forms of stress–strain behaviour obtained from pre-oriented (200%) *cis*-polybutadiene specimens in nitrogen, helium and sulphur dioxide environments at 93 K. Strain-rate $\simeq 10^{-3}$ sec^{-1}.
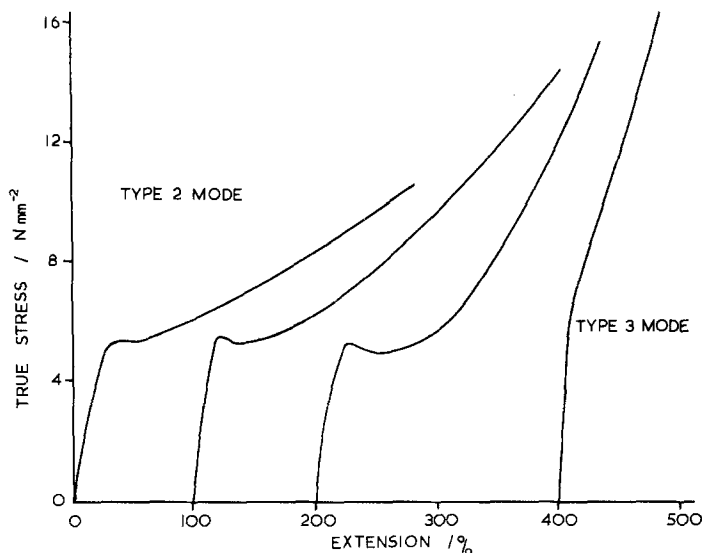
Figure 5 Stress—strain curves obtained from tensile testing polychloroprene at 203 K in a gaseous carbon dioxide environment. Intercept on the extension axis indicates pre-orientation applied at room temperature prior to low temperature testing.

pressure. No crazing was observed in contrast to that discovered by Imai and Brown for PMMA. However, the temperature of the test was above the T_g of polybutadiene. This observation suggests a second necessary criterion for environmental crazing, that the polymer must be tensile tested below its T_g.

When specimens having their T_g above 195 K are stretched in carbon dioxide at 195 K, environmental crazing is again observed. Stress—strain curves for polychloroprene obtained by tensile testing at 195 K in the presence of gaseous carbon dioxide are shown in Fig. 5. Various pre-test orientations were used as indicated by the intercept on the extension axis of Fig. 5. Several important points are noteworthy. Craze bands could again be observed for the 200% pre-oriented polychloroprene specimens. The bands were much broader than those formed in nitrogen and also much fainter. It is thought that this may be a consequence of the higher temperature of formation. The faintness of the bands indicated, as subsequent measurements verified, that the quantity of carbon dioxide gas absorbed by polychloroprene at 195 K was much less than the nitrogen absorbed at 77 K. Curves shown in Fig. 5 are true stress—strain curves, and it can be seen that, with pre-test orientation greater than 300%, the initial load drop at yield is absent. Similar curves to those shown in Fig. 5 have been previously observed with polyisoprene [18]. The ductile mode without crazing at high pre-orientation is also similar to that for highly oriented polybutadiene. Carbon dioxide

penetration in polychloroprene was markedly reduced when the pre-orientation exceeded 200%.

There are both similarities and differences in the crazing behaviour observed near 77 K in nitrogen for all the poly(dienes) tested and that for polychloroprene tested in carbon dioxide at 195 K. The similarity is that type 2 mode of deformation is observed at both temperatures. One difference has already been mentioned, that the bands formed in polychloroprene at 195 K were much broader than those formed at 77 K. A further difference is that the craze bands formed at 195 K in polychloroprene did not cover the entire cross-sectional area of the specimen, as was observed at 77 K in nitrogen. Fig. 6 shows an optical light micrograph of a thin section of one half of a polychloroprene sample that had crazed in carbon dioxide near 195 K. The photograph was taken very soon after the specimen had been warmed to room temperature. Even so, some gas had already escaped from the outer edges in the cutting and handling operation. The dark outer zone is a heavily cavitated region containing large quantities of gas. The centre has only a few gas-filled cavities. The photograph indicates that the crazes propagate from the outer surfaces of the sample towards the centre. Since the slice taken is of finite thickness, it is not known whether the crazes propagating from different edges are related or independent of each other and at different levels.

Another difference in the behaviour at the different temperatures is the pre-test orientation necessary for the transition from type 2 to type 3
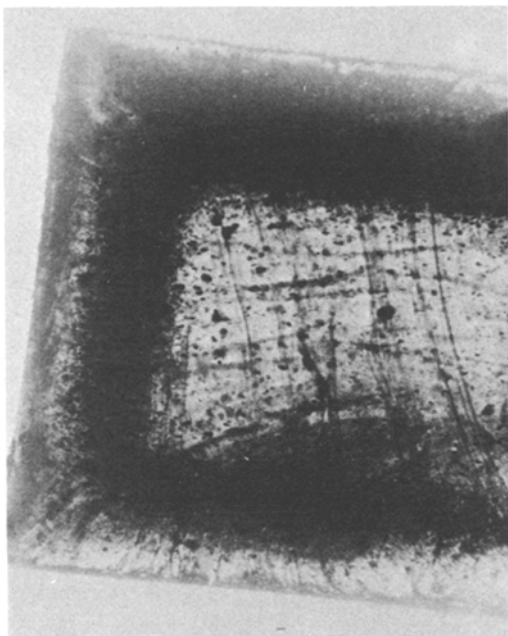
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Figure 6 Thin section of a tensile-tested polychloroprene sample which has crazed, viewed by transmitted light microscopy shortly after testing in carbon dioxide at 195 K. Section taken perpendicular to tensile axis and shows three outer edges of the complete cross-section.

behaviour. At 77 K in nitrogen the minimum pre-orientation to initiate type 3 behaviour is 400%, while at 195 K this is reduced to 200 to 300%. The region of craze behaviour on a pre-orientation—strain rate plot diminishes as the test temperature is raised from the liquefaction temperature of the environment. Craze growth is enhanced as the liquefaction temperature is approached, as is indicated by the increased quantity of gas absorbed.

5. Analysis of gases evolved from mechanically deformed polybutadiene specimens

The importance of the gas on the mechanical properties emphasizes the need for quantitative analysis of the environmental gas. Analysis of the gases evolved from the low temperature tensile-tested polybutadiene specimens, stretched at 83 K, was undertaken to assess:

(a) the quantity of gas liberated from the polymers at room temperature, assumed equal to the quantity of gas penetrated into the polymer during low temperature tensile testing;

(b) the volume ratio of the component gases evolved from the polymer at room temperature,

compared with the composition of the test environmental gases at low temperature.

5.1. Quantity of gas

In order to assess the quantity of gas evolved from the polymer after the low temperature tensile testing, the specimens were warmed from 77 K to room temperature in a vessel of known volume, which was connected to a mercury manometer. At 77 K the vessel was evacuated to a vapour pressure of 1 Torr, after pumping for 1 h. The vapour pressure was finite and persistent. It appears that the gases can be removed by pumping, but considering the large quantities absorbed only a small proportion will be removed during the initial pumping.

Fig. 7 shows the vapour pressure curve obtained from crazed polybutadiene samples warmed from 83 K to room temperature. Even at temperatures near 77 K, volatile constituents were evolved. However, the gas is not released in large quantities until the temperature is very close to the T_g of the elastomer. The rapid release of gas thus coincides with the transition from a glass to a rubber-like material and also with the rapid decay in radical concentration as previously reported [14]. The curve in
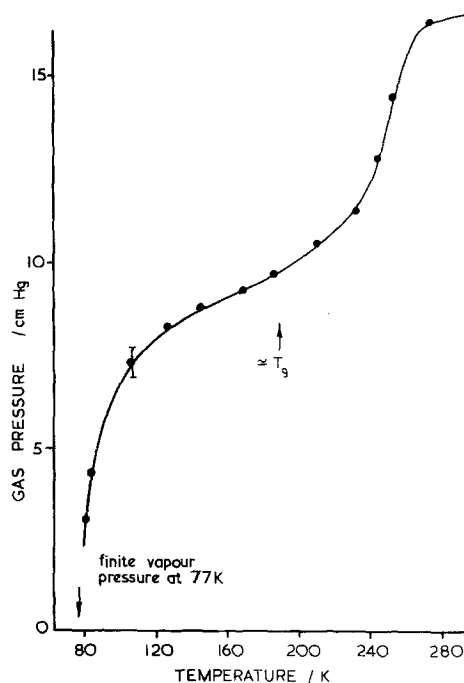

Figure 7 Variation in vapour pressure of gases evolved from *cis*-polybutadiene samples after tensile testing at 83 K. Data collected over a period of 2 to 3 days to approach equilibrium conditions.

856

Fig. 7 finally saturates to a constant value indicating the maximum pressure exerted by the total volume of gas evolved from the specimens in the vessel. The time taken for saturation was 2 to 3 days. Knowing the pressure of the gas and the volume of the gas collection apparatus, the volume of the gas evolved from the rubber specimens was determined.

Volumes of the order of $80 \, cm^3 g^{-1}$ of rubber were collected at room temperature. This poses the question of how such a quantity of fluid is stored at the test temperature. Clearly the gas cannot be held in gaseous form within the specimen at the test temperature, even allowing for the reduced volume at lower temperature. Since the crazing and gas penetration occur only at temperatures close to the liquefaction temperature of the test environment, one possibility is that the gas is stored as liquid within the craze cavities. Liquid nitrogen occupies only 10^{-3} of the gas volume at room temperature for the equivalent mass of gas. The observed gas volume at room temperature would thus occupy only $\approx 8\%$ of the sample volume if stored as liquid. If the gas is held as liquid, this raises a further problem of the nature of the driving force for liquefaction of the gas at temperatures above the normal liquefaction temperature. A further possibility for the gas storage mechanism is that it is stored as a monolayer on the surface of the craze cavities. A rough calculation shows that sufficient surface area for the number of gas molecules present in $80 \, cm^3$ of gas, could be arranged within the rubber.

There are possibly other mechanisms by which the large quantity of nitrogen can be accommodated. Polymers are known to contain free volume, probably sufficient to hold the gas molecules, although not enough to allow them the Brownian movement of the gaseous phase. Any discussion of the nature of the gas storage mechanism must be tentative.

A second experiment was performed using polybutadience specimens which had been highly oriented at room temperature and stretched at 83 K. The total gas volume collected at 20°C from these specimens was approximately $1 \, cm^3 \, g^{-1}$ confirming the observations that for highly oriented polybutadiene specimens deformed at 83 K, the crazing and gas/liquid penetration was drastically reduced.

5.2. Composition of gases evolved from low temperature tensile-tested polybutadiene specimens

The second analysis of the gas evolved from the low temperature tensile-tested polybutadiene specimens concerned the composition of the gas.

The method used for the analysis of the gas evolved from the polybutadiene specimens was decided by the availability of equipment. A mass spectrometer was used and the relative peak heights from the constituent gases were compared. Unfortunately, the method suffers from its inability to accurately access the component volume of gas in a sample.

Fig. 8 shows the relative peak intensity results of the mass spectrometer scans versus temperature for the gases evolved from a polybutadiene specimen. The peak intensities shown in Fig. 8 represent the various components of the gases evolved from the sample. The numbers on the curves refer to the mass numbers. The mass numbers for the ionized species H^+, H_2^+, O_2^+, OH^+, H_2O^+, N_2^+ are respectively 1, 2, 32, 17, 18 and 28.

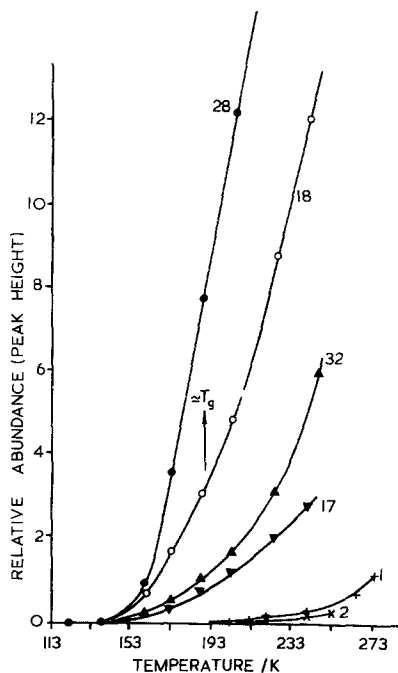It can be seen that the major constituents of the evolved gases are nitrogen, oxygen and water

Figure 8 Mass spectrometer data obtained by analysing gas constituents released on warming from cis-polybutadiene after tensile testing at 83 K.

vapour. The small amount of atomic hydrogen may be attributed to the ionization of water vapour. There is no evidence of large quantities of hydrogen being evolved, as was previously stated [4]. The small H_2 peak may be attributed to the water clearly present. The gases evolved may, therefore, all be attributed to the environments in which the specimens were prepared and the tensile tests conducted. The quantity of oxygen liberated from the polymer is approximately $\frac{1}{7}$ that of nitrogen by mass, or $\frac{1}{8}$ the nitrogen by volume. Since the tensile tests were conducted in a commercially pure nitrogen atmosphere, it is not surprising that the nitrogen forms the main constituent of the evolved gas. However, the relatively high oxygen content does provide plenty of oxygen for the formation of peroxy radicals where molecular chain scission occurs.

It is seen from Fig. 8 that the ratio of the relative abundance remains constant over the temperature range; no one gas being given off more readily than any other gas. Fig. 8 also shows that the gases are only liberated as the T_g of the rubber is approached and given off in large quantities only when the T_g is exceeded.

6. Reloading experiments

The above sections have considered the influence of the environment on the mechanical properties of the deformed polydienes. It has also been previously shown [3, 4] that radicals are produced during the crazing mode of deformation, which may be detected by ESR. The radicals result from main chain fracture within the polymer network. Any oxygen present in the test environment gives rise to peroxy radicals. In order to further assess the inter-relationship of test environment, mechanical behaviour and molecular fracture properties of the polybutadiene, a further set of experiments were conducted, termed repeat loading experiments. In these tests the samples were not tested to fracture, but subjected to two similar cycles of tensile testing, while the accumulation of absorbed gases, radicals and changes in mechanical behaviour on subsequent cycles was studied.

The method adopted for these tests was as follows:

(1) First the polybutadiene specimens were pre-strained by 200% and stretched at 83 K to an initial strain equal to, say 10%. At 10% strain the experiment was terminated and the number of

radicals or gas evolved from the specimens was measured. For these measurements the extended specimen had to be cut into several pieces. This meant that it was not practical to further restretch the specimens. This test, therefore, provided a comparison with the radical concentration measurements and the quantity of gas collected for a specimen which was to be restretched as described in (2) below.

(2) Test 1 was repeated but this time the specimen was allowed to warm to room temperature for 10 min without destroying the specimen by cutting it. This allowed any radicals formed to decay as evidenced by the absence of ESR spectra above the T_g of the rubber, and the specimen to return approximately to its initial length (2.5 cm). The radical concentrations produced in these specimens below T_g are assumed to be equal to those produced in specimens deformed as in (1) above. After the recovery period at room temperature, the specimen was pre-strained as previously and then restretched under the same test conditions, to the same degree of extension. The radical concentration was then measured at 123 K. This method was repeated for similar specimens with increased strains, for a range of strains from 10% up to that which caused fracture on the first loading and/or fracture on the second loading, since in either case direct comparison between the first and second loading results on the same specimen was not possible.

The results of such measurements are shown in Fig. 9. It is seen that the number of radicals per unit volume formed during the second loading is greatly reduced at all strain levels compared to the first loading. The reloading experiments demonstrate that cumulative damage of the sample by molecular fracture is irreversible, the majority of molecular fracture for a given extension occurring on the first deformation. Further support for the importance of increasing strain on the degradation of the network is given by the observation that during the second and third repeat loadings, the strain to fracture compared to the first loading was considerably reduced. Fracture was always obtained at the yield point on the third loading.

In contrast to the very reduced radical concentration on the second loading, the quantity of gas absorbed after the second loading is 2 to 3 times greater than on the first loading. Although the radicals decay rapidly on warming the specimen
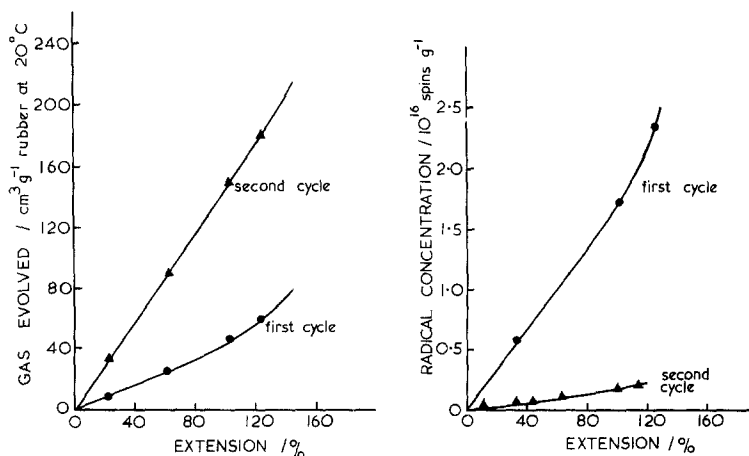
through T_g, the gas takes many hours to evolve completely from the specimen at room temperature, depending on its cross-link density. Hence very little gas would leave the specimen after the first cycle during the brief 10 min warm-up period. Consequently, gas absorbed during the second cycle is added to that already present from the first cycle. Further radical formation is detected when the strain in the specimen during the second loading exceeds that in the first loading [13, 19].

Fig. 10 shows the stress—strain curves for the first and second cycles of loading, for the case where crazing and gas absorption occur. The material generally follows the same stress—strain curve in each case, but there are significant differences. The initial modulus is less on the second cycle, presumably due to the presence of voids in the latter case. The presence or otherwise of fluid in the sample seems to have little effect on the
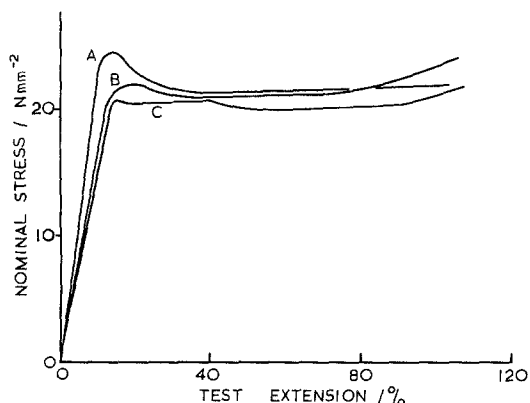

Figure 10 Comparison of stress—strain curves obtained from polybutadiene samples tensile tested at 83 K, strain-rate $\simeq 10^{-3}$ sec^{-1}. (a) Initial loading, (b) second loading retaining gas absorbed on the first loading, (c) second loading after allowing sufficient recovery time at room temperature for the absorbed gas to escape.

modulus. Secondly, the yield stress on the second cycle is reduced. Furthermore, if all the fluid is allowed to leave the sample before retesting, the drop in load at yield is virtually removed. The presence of fluid thus has some effect on the mechanical behaviour; possibly acting as some form of filler or providing internal stresses in the sample. The increasing load at large extensions on the second cycle is characteristic of the material being strained near to rupture.

7. Discussion

The factors which emerge from the experiments described and previous tests [11, 14] are as follows:

(a) Three modes of mechanical behaviour are observed with the diene polymers tested. The mode obtained is dependent on the degree of pre-test orientation, test strain-rate, cross-link density of the rubber and the nature of the environment in which the tensile test is conducted.

(b) One of the two ductile modes of mechanical behaviour appears to be associated with crazing.

(c) The crazing mode of behaviour is only observed when the test temperature is close to the liquefaction temperature of the environment and is below the glass transition temperature (T_g) of the rubber. The crazing mode is also only associated with the slower strain-rate tests, suggesting that a rate-dependent process is involved in the deformation mechanism.

(d) A large volume of the test environment gas is absorbed by the specimen, when the crazing mode of behaviour occurs. This gas is only subsequently released in large quantities from the specimen when its temperature is raised above the T_g of the polymer tested. The rate of gas release is

relatively slow (~hours) compared with the rate of radical decay at the T_g.

(e) Free radicals are formed in association with both ductile modes of behaviour. A high proportion of the radicals formed are peroxy radicals when oxygen is present in the test environment. It has been shown that the peroxy radicals are predominantly formed by association of the primary radical with oxygen in the test environment [14].

(f) On repeat testing of a specimen which has been initially tensile tested under conditions which produce crazing, the second cycle of loading produces virtually no more radicals but results in a considerably greater volume of absorbed environmental gas.

A full explanation of these factors is beyond the scope of one paper and interest is concentrated here on the possible mechanisms of environmental gas penetration into the sample when crazing occurs. The crazing mode of behaviour appears to be very similar to that observed in other glassy thermoplastics. The white striations, normal to the applied stress, visually appear identical to craze bands in glassy plastics. Furthermore they are load bearing even when they have traversed the full width of the specimen and "heal" on warming the material above T_g. In the case of the diene rubbers, the *visual* healing process is delayed by the time required for the escape of the entrapped gases. Indeed it is questionable whether a real healing of the voids occurs, since no further radicals are formed during the reloading tests. This can be interpreted by assuming that the radicals observed on the first loading result from chain rupture associated with the formation of the surfaces of the voids observed. Subsequent heating of the specimens above T_g results in the decay of the radicals, but not by recombination of the broken chains. On subsequent reloading, the initial void reopens without the breaking of further molecules and hence no new radicals are observed. This explanation assumes that the radicals observed during crazing are mainly associated with the formation of the large voids observed by optical microscopy. However, the distribution of radicals throughout a deformed specimen cannot be ascertained. Equal quantities of radicals are recorded from specimens which deform in a ductile manner without crazing and without absorbing gas. Hence only large (ductile) deformation of the network structure appears to be necessary for molecular rupture and radical formation. The radicals observed during crazing may be associated with the observable void formation, but could equally be associated with ductile deformation of the material around the void during its formation. Hence the observed radicals are not necessarily located only at the surface of the voids in crazed material. Since peroxy radicals are formed in the present case by the reaction of oxygen from the environment with the primary radical species formed by main chain scission [14] the site of molecular fracture must have a volume at least equal to that of an oxygen molecule.

Comment has already been passed on the large quantity of gas absorbed by the specimen when crazing occurs. While a small quantity of gas is absorbed during tensile testing by polybutadiene specimens which have been highly oriented at room temperature, large quantities (~80 cm³ g⁻¹ of rubber) are only obtained from specimens which exhibit crazing. This quantity is markedly increased by repeat loading of the specimen. Since large quantities of gas are only absorbed by specimens which exhibit visual crazing, it is tempting to assume that the fluid absorbed is stored in the voids of the crazes. However, the exact location of the stored gas has not been unequivocably determined.

Two suggestions have already been made concerning mechanisms for storing the large quantities of gas within the specimens, these are liquefaction of the gas and the possible formation of an adsorbed layer on the surface of the craze cavities. Crazing and gas absorption occur at temperatures close to the liquefaction temperature of the environment and over a short temperature range (~30 to 40 K) above the liquefaction or sublimation temperature. Gas absorption increases as the liquefaction temperature is approached. These connections of the observed phenomena with the liquefaction temperature suggest that the large quantities of gas could be accommodated as liquid within the craze cavities. Once formed as liquid, capillary effects could serve to retain the fluid and thus prevent its rapid release. If liquefaction of the gas is considered remotely from any possible interaction with the rubber, the problem then arises of the nature of the driving force for liquefaction of the gas at temperatures greater than the liquefaction temperature at normal pressure.

Fig. 11 shows the pressure needed to liquefy nitrogen as the temperature is increased above 77 K and for the sublimation of carbon dioxide.
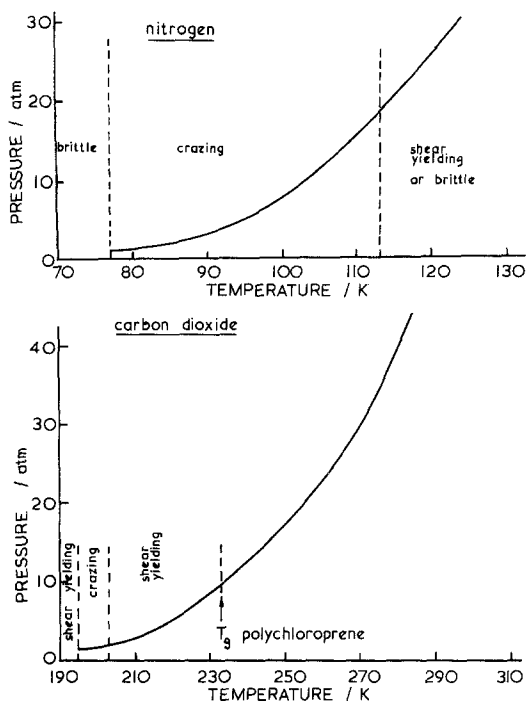
Figure 11 Liquefaction/sublimation thermodynamic data for nitrogen and carbon dioxide, with superimposed temperature zones indicating the mechanical behaviour obtained from pre-oriented diene rubbers for polybutadiene (above) and polychloroprene (below) in low strain-rate tensile tests at 1 atm external pressure.

Fig. 11 also shows the temperature ranges in which crazing is observed in the poly(dienes) in both nitrogen and carbon dioxide gas. While the temperature band for crazing in nitrogen is reasonably extensive ($\simeq 50\,K$) that for carbon dioxide is very narrow ($\simeq 10\,K$). Furthermore the temperature for the transition from crazing to shear yielding corresponds to a pressure for liquefaction of the gas of about 18 atm in nitrogen, but only about 1.5 atm in carbon dioxide. The exact role of the vapour pressure on crazing near the liquefaction temperature of the environmental gas is, therefore, difficult to ascertain. It is difficult to conceive of the nitrogen gas being subjected to 18 atm to cause liquefaction of the gas. However, the vapour pressure of the environmental gas plays some part in the crazing process, since the amount of gas absorbed and the likelihood of crazing increases as the liquefaction temperature at normal pressure is approached.

This simple concept of liquefaction of the gas in the craze cavities would explain the storage of large quantities of gas but does not explain why a further large quantity of gas is absorbed during reloading tests, when the radical concentration data suggest that the original holes merely reopen. It is possible that the gas collected on the first cycle is able to diffuse into the rubber easily when it is warmed above T_g, thus allowing room for more gas absorption on the second loading. However, rapid diffusion of the gas into the uncrazed material at temperatures above T_g should then be observed in both crazed and uncrazed materials alike. Since significant diffusion of gas into uncrazed specimens is not observed, the diffusion theory does not seem a reasonable explanation of greater absorption during reloading tests.

It is also possible to explain the quantity of gas stored by the polymer at low temperature by postulating that physical adsorption occurs within the voids. Adsorption of a gas on the polymer would be spontaneous and must be accompanied by a decrease in the free energy, ΔF, of the system. This view is supported by the work of Graham, who showed that at temperatures near the boiling point of liquid nitrogen and at 1 atm pressure, the surface energy of the polymer is reduced by approximately $10^{-2}\,J\,m^{-2}$ [20, 21]. It is possible that free radicals at the surface of the voids, formed as a result of molecular rupture, provide an active surface on which a monomolecular layer of condensed gas forms and further physical adsorption of gas then occurs. While this might explain the large amount of gas stored, it does not explain why crazing occurs in the first instance and why crazing is only observed near the liquefaction temperature of the environment. The reduction in surface energy of the polymer at temperatures near the liquefaction temperature, as shown by Graham [20, 21], may account for the occurrence of void formation and hence crazing only at these temperatures. Crazing in this event is clearly environmental crazing and would be controlled by the rate of diffusion of gas into the polymer, so reducing its surface energy. This would explain why crazing is only observed in tests conducted at low strain-rates, when sufficient time exists for the diffusion processes.

A brittle mode of fracture is observed when the specimens are tested at 77 K in helium. Helium has a boiling point of 4.2 K and is, therefore, well above its liquefaction temperature at 77 K. Consequently, the crazing mode of behaviour cannot occur.

8. Conclusions

It has been demonstrated that the cross-linked

861

polydienes exhibit various modes of deformation dependent on the test temperature, pre-test orientation, test strain-rate, cross-link density of the specimens and the environment in which the specimens are tensile-tested. The source of the evolved gas from the low temperature tensile-tested samples warmed to room temperature is environmental. The modes of deformation which have been observed are:

(a) a brittle mode of deformation observed for lightly pre-oriented samples stretched at high strain-rates or at low temperature and/or using an environmental gas which does not liquefy near the test temperature;

(b) a crazing mode of deformation which is partially controlled by the temperature and pressure of the gaseous environment in which the specimen is stretched. This crazing mode may be observed in the poly(dienes) providing the specimen is deformed below its T_g, and is close to or at the liquefaction conditions of that environment. The exact role of the absorbed gas on crazing has still to be ascertained;

(c) a ductile mode of deformation for high pre-test orientation which is independent of the environment in which the poly(dienes) are stretched, and independent of the test temperature and applied strain-rate.

The results of the reloading experiments in which crazing occurs may now be briefly concluded. During the first loading, voids and microcracks are irreversibly formed, which are associated with molecular chain rupture, the formation of free radicals and the absorption of considerable quantities of environmental gases. During the second loading, the voids are simply reopened, without the formation of significantly more free radicals, but with the penetration of further gas. The large quantities of gas stored in the material during both cycles is possibly held as an adsorbed layer on the surface of the voids. However, the exact mechanism of gas storage has not been unequivocably identified. The quantity of radicals and quantity of gas formed in the poly(dienes) during the first and second loading are not comparable. The number of gas molecules collected at 83 K from polybutadiene fractured specimens is $\approx 10^{22}$ g^{-1} of rubber, since 80 cm^3 g^{-1} of gas is collected at room temperature. If this is compared with the number of radicals produced at low temperature ($\approx 10^{16}$ g^{-1}) then it can be seen that the two quantities differ by several orders of magnitude.

Hence there does not appear to be a simple relationship between the two quantities and it is questionable whether the radical formation and gas absorption are critically interrelated or merely two simultaneous but discrete processes. Molecular rupture must be associated with void formation, but further chain scission may be associated with the general straining of the network away from the larger voids. The presence of free radicals at the surface of the voids could act as a key for gas adsorption.

Acknowledgements

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