JOURNAL OF MATERIALS SCIENCE 12 (1977) 2435–2440

The electric strength of copolymers

H. SABUNI, J. K. NELSON
Department of Electrical and Electronic Engineering, Queen Mary College, Mile End Road, London, UK.

Careful measurements of the electric strength of styrene–butadiene copolymers together with their parent homopolymers over a wide range of temperature are presented. The marked reduction of strength characteristic of a non-polar amorphous material occurs at a temperature indistinguishable from the glass transition temperature determined by differential thermal analysis. This temperature may be predicted from the constitution of the copolymer. The underlying mechanism is discussed in terms of molecular structure and movement.

1. Introduction

The electric strength of polymeric materials cannot be uniquely defined. Electronic theories of intrinsic breakdown developed to describe the situation relating to highly crystalline materials [1] display shortcomings when applied to many polymers. Specifically, the hypothesis of an electron–electron interaction is not always adequate to describe the abrupt changes in electric strength which occur in polymers as a function of temperature [2]. Furthermore the temperature at which the marked reduction in breakdown strength occurs for non-polar materials is not always shifted in the manner expected by the introduction of foreign atoms as trapping centres.

Research carried out on the dielectric, mechanical and viscoelastic properties of polymers [3] has highlighted the important effects of the systematic change of molecular structure on these physical properties. Chain substitution, cross-linking and copolymerization are obvious examples. Following this example a range of butadiene–styrene copolymers, together with their parent homopolymers were chosen for study. Molecular changes in these materials may be brought about by altering the amount of bound styrene which is reflected in the temperature characteristics. These elastomers are typical amorphous materials whose physical properties are uncomplicated by the presence of crystallites or polar groups.

2. Copolymer characterization

The materials used in this investigation were supplied by Phillips Petroleum (UK) and some of their known properties are tabulated in Table I. Although the basic microstructure of butadiene–styrene is well known, it was necessary to establish the degree of heterogeneity of the copolymers used. This necessity emerged from the fact that

TABLE I Physical properties of butadiene–styrene copolymers together with their parent homopolymers

Property	Polybutadiene Solprene 250*	Butadiene–styrene copolymer (Block) Solprene 1205*	Butadiene–styrene copolymer (Partial Block) Solprene 303*	Polystyrene Gosden 510*
Bound Styrene (%)	0	25	48	100
Block Styrene (%)	–	18	11	–
Density (gm cm^{-3})	0.895	0.930	0.970	1.04
Raw Viscosity at 100° C (ML-4)	47	52	48	–
Volatile Matter (%)	0.6	0.6	0.6	–

*Trade name.

the two copolymers contained a certain amount of styrene in block form; a matter which could affect their electrical properties since departures from the ideal random copolymer are known to be reflected in changes in the dynamic mechanical loss peak [4].

2.1. Infrared spectroscopy

Some evidence of the extent of the block structure may be obtained from the far infra-red spectrum [5]. The absorption bands occurring at 10.35 and 10.98 μm are associated with the butadiene 1.4- and 1.2-addition respectively, and those at 13.2 and 14.3 μm are associated with the phenyl groups [6]. However, the band at 18.5 μm in the far infrared can be attributed to rotational modes of the styrene blocks. The 75/25 copolymer exhibits a greater absorption at this wavelength than was evident for the 52/48 material despite the greater proportion of bound styrene in the latter. This qualitatively confirmed the heterogeneity inferred from Table I.

2.2. Differential thermal analysis (DTA)

The temperature of the glass–rubber transition of the four materials investigated was estimated by detecting the associated differential endothermic changes with respect to an inert reference as the temperature was increased at a rate of 5° C min^{-1}. This measurement was carried out on 6 mg samples using a Dupont-900 thermal analyser for temperatures in the range ± 100° C.

The DTA results in the form of thermograms are shown in Fig. 1, where a correction has been made for the Chromel–Alumel thermocouples used. The constructions shown by broken lines provide estimates of the glass transition temperatures (T_g) which are reproducible to within ± 1° C.

3. Electric strength measurements

3.1. Specimen preparation

The materials were prepared in sheet form by subjecting them to a pressure of 6.4 MN m^{-2} at 135° C between Melinex foils. After cooling under pressure, the resulting 1 mm sheets were recessed using a device similar to that described previously [7]. Recesses were formed by a highly polished stainless steel sphere 6 mm in diameter. This was pressed to a preset depth into 25 mm diameter samples of the prepared sheet at a controlled temperature of 135° C. Both polystyrene and elastomer specimens were prepared in this manner, although in the case of the latter preliminary roll milling at 50° C was undertaken. The Melinex foils were retained in the case of elastomer specimens to facilitate handling. Removal of the specimens from the recessing press was accomplished by cooling in liquid nitrogen vapour to achieve solidification of the rubber.

By placing a calibrated 2 mm sphere at the

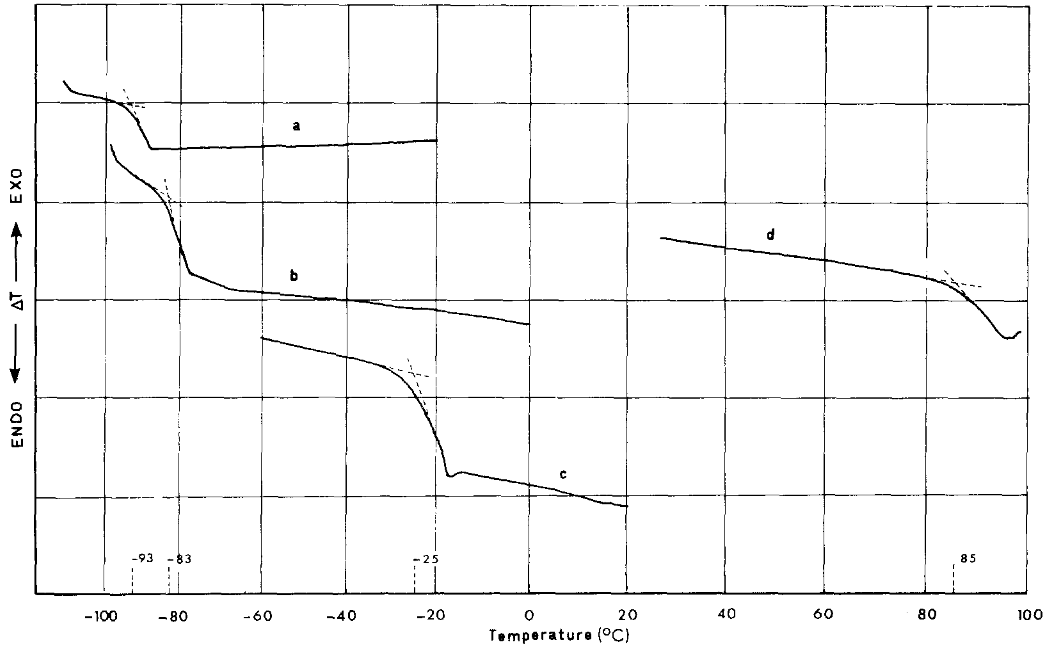

Figure 1 DTA thermograms; (a) polybutadiene, (b) 75/25 copolymer, (c) 52/48 copolymer, (d) polystyrene.

bottom of the recess the thickness of the specimens was measured using a vernier micrometer in conjunction with a travelling microscope to avoid distortion of the elastomer during measurement. All specimens were microscopically examined before testing and imperfect samples rejected.

3.2. Test cell and test procedure

Electric strength measurements of the recessed specimens were carried out in a temperature-controlled test cell. Samples were held by light spring pressure between sphere/plane electrodes of 6 and 10 mm diameter respectively. For polystyrene, vacuum evaporated films were applied to both sides of the specimen to ensure good contact. In the case of the elastomers the nature of the material precluded this technique, and reliance was placed on the good adhesion of the sphere electrode in the recess and a previously applied 9 mm diameter aluminium foil serving as a plane electrode. The supporting sphere electrode was polished after every breakdown.

In the temperature range —70 to + 110° C, silicone fluid was used as an immersion medium. Below —70° C, atmospheric air was found to be adequate. Temperature measurements were made using Chromel—Alumel thermocouples.

Direct voltages were applied from a high impedence source in the form of an increasing ramp function such that breakdown occurred in about 30 sec.

3.3. Results

Electric strength results for the four materials examined are shown in Fig. 2 as a function of temperature. The points on these curves represent the mean of the number of specimens designated at each point and the vertical lines indicate the corresponding standard deviations. Only those samples which exhibited failure at the point of maximum stress have been included. The critical temperatures (T_c) at which a marked reduction in strength occurred are also indicated. Fig. 2d for polystyrene is typical of a linear non-polar polymer, in which the strength is constant up to a critical temperature and falls rapidly above it. The elastomers, Fig. 2a, b and c, show similarities although the electric strength is not constant below the critical temperature and generally exhibits a plateau region above it.

Fig. 3 shows that both the homopolymers and the copolymer have a linear gap-dependence at room temperature, which when extrapolated passes through the origin. This behaviour justifies confidence in the meticulous sample preparation techniques adopted.

Any attempt to assess the effect of copolymerization on the magnitude of the electric strength can only be valid if the materials are in the same physical state. A comparison of the materials under investigation was made at liquid nitrogen temperature (— 195° C) at which all the materials are in the glassy state. The results are given in

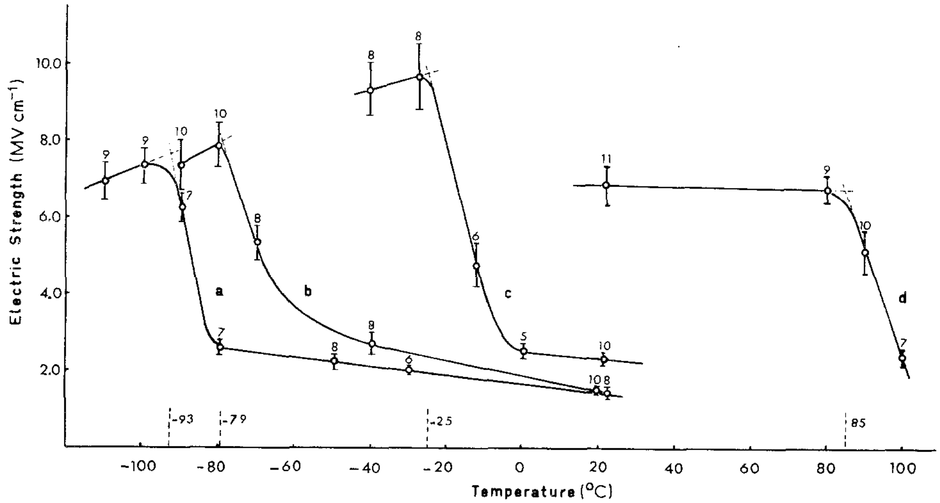

Figure 2 Electric strength as a function of temperature. Vertical lines indicate standard deviations and numerals indicate number of samples used in generating the mean. (a) polybutadiene; (b) 75/25 copolymer; (c) 52/48 copolymer; (d) polystyrene.

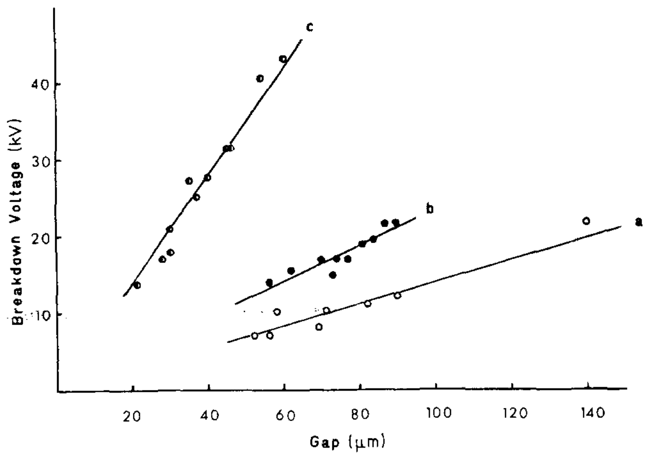

Figure 3 Breakdown voltage as a function of specimen thickness at 21° C. (a) polybutadiene; (b) 52/48 copolymer; (c) polystyrene.

Fig. 4. Since copolymers with more than 48% bound styrene were not available, some interpolation (shown dotted) has been necessary. The peak in the characteristic is further discussed in Section 4.

4. Discussion

The outstanding feature of the results presented is that critical transition temperatures obtained from electric strength measurements (Fig. 2) are synonymous with the glass transition temperatures derived from DTA (Fig. 1). The physical state of a polymer is markedly dependent on its glass transition temperature, whose value is influenced by a number of molecular parameters, such as the cohesive energy density, the flexibility of the chain backbone and the size and symmetry of substituted side groups. It is also to be inferred, therefore, that there is a considerable significance of the microstructure and morphology of a polymer in determining its electric strength [8]. Furthermore, molecular relaxation processes will be important in dictating the change of electric strength with temperature, and on this basis a marked change in strength at T_g could be expected.

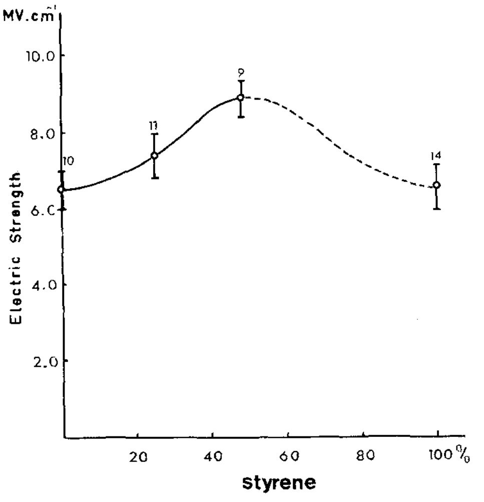

Figure 4 The variation of electric strength of butadiene–styrene copolymers with styrene content at – 195° C.

The hypothesis that molecular motion is largely responsible for determining the electric strength is also supported by the nature of the changes in strength depicted in Fig. 2. The high internal molecular mobility of polybutadiene and other rubbers, resulting from a flexible chain backbone, causes a decrease in their rotational energy barriers. This causes a reduction in electric strength at characteristically low temperatures. Conversely the bulky substituted phenyl groups in polystyrene will restrict the molecular mobility due to steric hindrance yielding a high critical temperature of 85° C. It is also apparent that the presence of styrene monomer in the copolymers studied had the effect of raising the transition temperature for the same reason. A similar explanation may be advanced for the temperature-independence of the electric strength of the elastomeric materials above T_g. In this region, physical entanglements between different chain segments (temporary crosslinking) can restrain the mobility of a high molecular weight polymer [9].

The variation of both the glass transition temperature, T_g, and the temperature, T_c, for the rapid fall in electric strength has been plotted in Fig. 5 as a function of the percentage of bound styrene in the copolymer. Glass transition temperature measurements by Tobolsky [10] and Wood [11] in randomly distributed copolymers

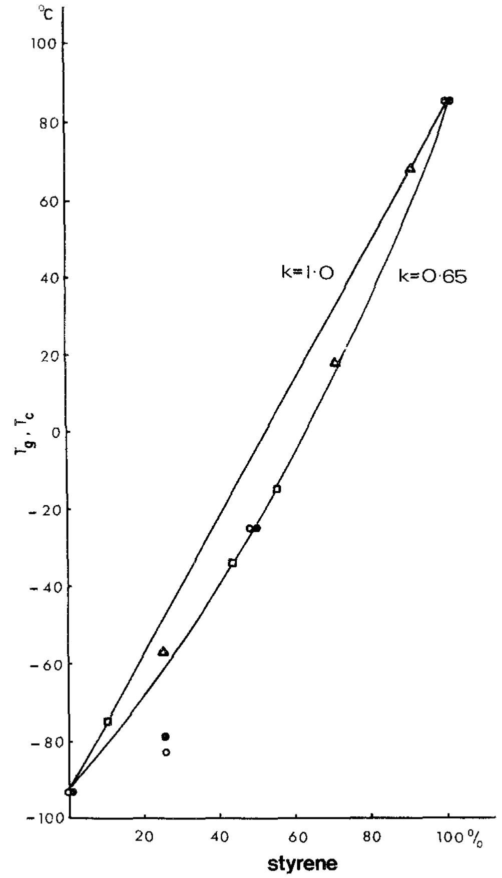

Figure 5 The variation of T_g and T_c of butadiene–styrene copolymers with styrene content: ● T_c present work; ○ T_g present work; □ T_g experimental after Wood [12]; △ T_g experimental after Tobolsky [11]; — T_g theoretical after Wood [12] (Equation 1).

formed by emulsion polymerization have been included for comparison. It has been shown [11] that the composition dependence of the glass transition temperature, T_g, of a truly homogeneous binary copolymer may be estimated from

$$(1 - w_2)(T_g - T_{g1}) + kw_2(T_g - T_{g2}) = 0, \quad (1)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the two constituent homopolymers, w_2 the weight fraction of component 2 in 1, and k is an experimental constant less than unity. It may be seen from Fig. 5 that most of the experimental data are in good agreement with Equation 1 for $k = 0.65$. The exception is the 75/25 copolymer. In view of the indications of Section 2.1 it is likely that this anomaly is due to the block structure of the 75/25 material. However, the fact that both T_g and T_c are lower than predicted by Equation 1 adds credence to the proposition that both properties are dependent on the same molecular parameters.

Most previous explanations [12, 13] of the electric strength of polymers have relied on an extension of the ideas of von Hippel [1] for the intrinsic breakdown of organic crystals. This approach [12], identifies T_c not with the glass transition temperature, but with the temperature at which electron–electron interaction becomes as important as the collisions between conduction electrons and the lattice of the material. One of the predictions made on this basis is that T_c should be decreased by the introduction of foreign atoms or ions. In support of this idea, Oakes [13] has shown that a lowering of T_c may be achieved for polyethylene by chlorinating the polymer. In this case the introduction of a polar group is thought of as giving rise to additional scattering and electron energy loss. This type of explanation is not altogether adequate, however, to explain the present results, since the introduction of styrene into the elastomeric matrix has the opposite effect. Furthermore, the presence of foreign molecules tends, according to Fröhlich's theory [12], to increase the electric strength in the low temperature region and to effect a decrease at high temperatures. The strengths of the copolymers are, however, higher than that of the polybutadiene over the entire temperature range. Other inconsistencies in the high-temperature region have also been observed for inorganic materials [14].

In view of the intimate relationship shown between T_g and T_c it is suggested that the molecular structure and motion is of paramount importance in determining the electric strength [8]. Following the work of Artbauer [15], it is likely that a nonpolar amorphous polymer will fail electrically when the energies acquired by accelerated electrons increase to a critical value after transit through voids present in the material. In this way the extent of the free volume exhibited by the structure assumes considerable importance, and the marked reduction in strength evident at T_g may be understood in terms of the loosening of the molecular structure.

The effect of copolymerization on the low temperature electric strength (Fig. 4) is very similar to the behaviour reported by von Hippel [16] in a mixed crystal system, in which the replacement of KCl by RbCl increased the electric strength up to a point after which it decreased again towards the strength of RbC1 when the replacement was completed. In view of the marked similarity, the applicability of a Fröhlich type of theory at low temperatures seems reasonable, although electron scattering does not present an adequate explanation for the observed fall in strength.

However, Ferry [17] has tabulated approximate values of percentage free volume as follows:

Polystyrene	0.032–0.033
Polybutadiene	0.039
76.5/23.5 random copolymer	0.021

The fact that the copolymer presents less free volume than either of its homopolymers may also be used to explain the maximum exhibited in Fig. 4 on the basis of the ideas previously outlined above.

Acknowledgements

The authors are indebted to the University of Damascus for the provision of a study grant (H.S.). Thanks are also due to Phillips Petroleum for the provision of samples, and the Department of Materials at QMC for help with polymer moulding and DTA.

References

1. A. VON HIPPEL, *Z. Phys.* **67** (1931) 707.
2. J. H. MASON, *Progress in dielectrics* **1** (1959) 3.
3. K. A. WOLF, *Z. Eleckrochem.* **65** (1961) 604.
4. M. MATSUO, T. UENO, H. HORINO, S. CHUJYO and H. ASAI, *Polymer* 9 (1968) 425.
5. G. KRAUS, C. W. CHILDERS and J. T. GRUVER, *J. Appl. Polymer Sci.* **11** (1967) 1581.
6. H. W. THOMPSON and P. TORKINGTON, *Trans. Farad. Soc.* **41** (1945) 246.
7. A. E. W. AUSTEN and H. PELZER, *J. IEE* **93** (1946) 525.
8. H. SABUNI and J. K. NELSON, *J. Mater. Sci.* **11** (1976) 1574.
9. F. BUECHE, "Physical Properties of Polymers" (Interscience, New York, 1962) p. 212.
10. A. V. TOBOLSKY, "Properties and Structures of Polymers" (Wiley, New York, 1960) p. 800.
11. L. A. WOOD, *J. Polymer Sci.* **28** (1958) 319.
12. H. FRÖHLICH, *Proc. Roy. Soc.* **188A** (1947) 521.
13. W. G. OAKES, *Proc. IEE* **96A** (1949) 37.
14. R. COOPER, *Progress in Dielectrics* **5** (1963) 95.
15. J. ARTBAUER, *Kolloid Z. u. Z. Polym.* **202**(*i*) (1965) 15.
16. A. VON HIPPEL, *Z. Phys.* **88** (1943) 358.
17. J. D. FERRY, "Viscoelastic properties of polymers" (Wiley, New York, 1970) p. 316.

Received 14 February and accepted 11 March 1977.