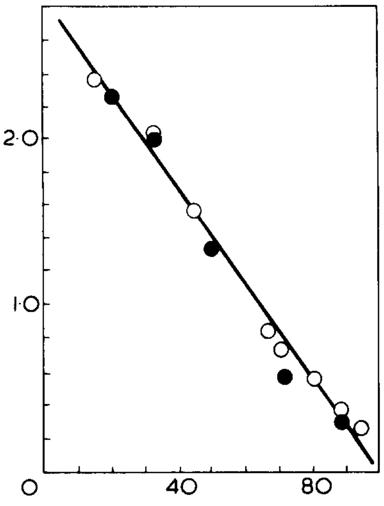

Figure 3 A calibration line obtained by plotting the ratio of the absorbance of the band at 1550 cm^{-1} to that of the band at 2878 cm^{-1} (A_{1550}/A_{2878}) against the degree of deacetylation. (●), I.r. data of the samples made by the homogeneous hydrolysis; (○), those of the samples obtained by the heterogeneous hydrolysis

derived from the i.r. data obtained from the two series of partly deacetylated chitin samples prepared by the heterogeneous and homogeneous hydrolyses, respectively. The interesting comparison is that the slopes of the lines A and B are appreciably different from each other. We have already reported that the structures of the chitin congeners would be different from each other, depending on the hydrolysis mode[5]. The difference in the slopes of the Beer–Lambert lines A and B in *Figure 2* may reflect sensitively the difference of the structures of the chitin congeners.

Very similar phenomena have been reported to be observed in the estimation studies of the acetyl content of cellulose acetate[10]. The Beer–Lambert curves for the intensity of the C=O stretching band were known to give different slopes depending on the difference in acetylation procedures. O'Connor suggested that the difference in slopes might be a clue to the position or site of the chemical modification[10]. This suggestion is quite similar to our view about the structural difference of the chitin congeners.

Figure 2 shows considerable scatter probably due to some experimental errors including that in weighing, as chitin and its congeners are very hygroscopic. In order to correct the errors, the absorbance of the amide II band at 1550 cm^{-1} was divided by that of C–H band at 2878 cm^{-1} which was previously confirmed not to be affected by the deacetylation.

Figure 3 depicts the plot of the ratio of the absorbance of the amide II band at 1550 cm^{-1} to that of the band at 2878 cm^{-1} against the degree of deacetylation. As can be seen from *Figure 3*, the correction technique gave data which showed considerable decrease in scatter of the points about the calibration line. More attractive is the fact that the plot resulted in a single linear relationship for both partly deacetylated chitin samples made by the homogeneous and heterogeneous deacetylation. This single relationship appeared to correspond well to that of the cellulose acetate case, which made the determination of acetyl content in any cellulose acetates accurate[11].

The results obtained above indicate that with this calibration technique, the degree of deacetylation of any partly deacetylated chitin samples can be estimated rapidly with satisfactory precision and accuracy regardless of the deacetylation mode.

REFERENCES

1 Muzzarelli, R. A. A. 'Natural Chelating Polymers' Pergamon Press, New York, 1973, pp.177–227
2 Sannan, T., Kurita, K. and Iwakura, Y. *Makromol. Chem.* 1975, **176**, 1191
3 Sannan, T., Kurita, K. and Iwakura, Y. *Ibid.* 1976, **177**, 3589
4 Kurita, K., Sannan, T. and Iwakura, Y. *J. Appl. Polym. Sci.* in press
5 Kurita, K., Sannan, T. and Iwakura, Y. *Makromol. Chem.* 1977, **178**, 2595
6 Kurita, K., Sannan, T. and Iwakura, Y. *Ibid.* 1977, **178**, 3197
7 Hackman, R. H. *Aust. J. Biol. Sci.* 1954, 7, 168
8 Elek, A. and Harte, R. A. *Ind. Eng. Chem. (Anal. Edn)* 1936, **8**, 267
9 Pearson, F. G., Marchessault, R. H. and Liang, C. Y. *J. Polym. Sci.* 1960, 43, 101
10 O'Connor, R. T. 'Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose' Marcel Dekker, New York, 1972, p 420
11 Hurtabise, F. G. *Tappi.* 1957, 45, 460

Determination of the solubility parameter of o-hydroxypropyl cellulose

George A. F. Roberts and Iwan M. Thomas
Department of Physical Sciences, Trent Polytechnic, Burton Street, Nottingham NG1 4BU, UK
(Received 15 August 1977; revised 20 October 1977)

INTRODUCTION

A polymer is normally soluble[2] only in liquids whose solubility parameter values fall within the range $\delta_p \pm 3.0$ Hildebrands, the solubility decreasing with an increase in the difference between δ_p and δ_L. *o*-Hydroxypropyl cellulose with an *MS* of approximately 4.0 exhibits solubility[3] in liquids over a much wider range of δ values, from water ($\delta = 23.4$) to piperidine ($\delta = 8.7$) and having widely differing hydrogen bonding abilities and polarities, e.g. water, dimethylformamide and chloroform.

In view of the wide solubility spectrum of this polymer the value of δ_p has been determined, using the maximum limiting viscosity number (*LVN*) method[2]. In addition δ_p has been calculated directly using Small's technique[4], and has been determined by a novel method based on surface tension measurements[1].

EXPERIMENTAL

The *o*-hydroxypropyl cellulose used was an unfractionated commercial sample (Klucel MF produced by Hercules Inc,) with a nominal *MS* value of 4.0. The solvents were either Analar grade or purified by distillation prior to use. Viscosities were measured at 25.0° ± 0.05°C, and the surface tension measurements were carried out using a Du Noüy balance.

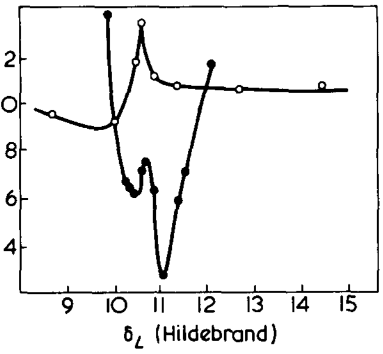

Figure 1 The *LVN* of solutions of *o*-hydroxypropyl cellulose as a function of the solubility parameter of the solvents: ○, strong hydrogen bonding solvents; ●, DMF/THF mixtures

RESULTS AND DISCUSSION

Four experimental determinations of δ_p were carried out, two by the maximum *LVN* method and two using surface tension measurements. Both strong and moderate hydrogen bonding solvents were used with each method.

Measurement of maximum LVN

The strongly hydrogen bonding solvents used in the viscosity study, together with their δ_L values in parentheses, were water (23.4), methyl alcohol (14.5), ethyl alcohol (12.7), n-butyl alcohol (11.4), sec-butyl alcohol (10.8), tert-butyl alcohol (10.6), isobutyl alcohol (10.5), isoamyl alcohol (10.0), and piperidine (8.7). The *LVN* values are plotted against the δ_L values in *Figure 1;* from these a value of δ_p = 10.65 Hildebrands is obtained.

Two moderate hydrogen bonding solvents, tetrahydrofuran (9.9) and dimethylformamide (12.1), were used together with mixtures of these two solvents. The values of the solubility parameter for the mixtures were calculated using the equation:

$$\delta_L = \delta_{mix} = \delta_1 V_1 + \delta_2 V_2$$

where V_1 and V_2 are the fractional volumes of solvents 1 and 2, respectively[2]. The *LVN* values are plotted against the δ_L values in *Figure 1.* The graph has an unusual shape, the *LVN* being greater in the two pure solvents than in any of the intermediate mixtures. Normally the *LVN* values in mixed solvents are either intermediate between those in the pure solvents or exhibit a maximum. It was originally thought that since the minimum occurs at a solvent composition of approximately 1:1, the two solvents were preferentially hydrogen bonding to each other, thereby reducing the solubilizing power of the mixture relative to that of a single solvent of moderate hydrogen bonding ability and similar δ_L value. However, the *LVN* of the polymer in *N,N*-dimethyl acetamide (δ_L = 10.8) was found to be 7.4 dl/g, similar to that for the mixed solvent having δ_L = 10.8. Thus the shape of the curve cannot be due to preferential hydrogen bonding between the two components of the solvent mixtures. The curve has a peak at a value of 10.7 Hildebrands which is in good agreement with the value obtained with solvents of strong hydrogen bonding ability.

Calculation of δ_p *by the method of Small*[4]

Small's method is based on the assumption that the contributions of the individual atoms or groups to the overall value of the solubility parameter of the molecule are additive. Small calculated molar attraction constants (F) for a wide range of atoms and groups and using these the solubility parameter can be calculated from the formula:

$$\delta_p = \Sigma F.d/\text{Molecular weight}$$

where d is the density of the polymer.

Using a value of 1.170 for the density[5] and a value of F_{OH} = 380, similar to that for the secondary hydroxyl group in isopropyl alcohol, the calculated value for *o*-hydroxypropyl cellulose is 10.2 Hildebrands. This is less than the values obtained experimentally by the maximum *LVN* method. However, the experimental determinations involved strong or moderate hydrogen bonding solvents whereas Small's method assumes no specific solvent–polymer interactions. Examination of the δ_p values of a number of polymers[2,6] shows that there is, on average, a decrease in δ_p with decrease in the hydrogen bonding capability of the solvents used in the determination. The average decrease on going from strong to poor hydrogen bonding solvent systems is 1.7 Hildebrands. Thus, the calculated value for δ_p would be expected to be less than the experimentally determined value when using solvents capable of hydrogen bonding with the polymer.

Determination of δ_p *from surface tension measurements*

This method is based on the assumption that the poorer the solvent for the polymer the greater will be the tendency of the polymer to move to the air–solvent interface. Therefore the difference between the surface tension of the solution and that of the solvent should be a minimum where δ_p and δ_L most closely match. The surface tensions of the solvents were determined, then those of the corresponding 0.75% (w/v) solutions of polymer. Two solvent systems, acetone/water and DMF/THF, were used and the surface tensions of both varied linearly with composition whilst those of the solutions passed through a minimum. The plots of $\Delta\gamma$ against the solubility parameter of the solvent are shown in *Figure 2.* For the acetone/water system the minimum occurs at 10.9 Hildebrands and at 10.6 Hildebrands for the DMF/THF system. Both are in very good agreement with the values obtained by the *LVN* method. The agreement is encouraging but it may be fortuitous, as the validity of the method has yet to be established. It is intended to examine the technique further to determine the reliability, as it has the advantage of being considerably quicker than the *LVN* method.

In all cases the surface tensions of the solutions were greater than those of the corresponding solvents, contrary to the normal situation in which the solution surface tension is lower. One possible explanation is that the technique is measuring the 'surface tension' of the polymer, lowered by the presence of solvent molecules. This is supported by the fact that although the surface tensions of THF and acetone differ considerably, the values for the solutions of *o*-hydroxypropyl cellulose are 30.2 and 30.3 mN/m, respectively, identical within the limits of experimental error. Since THF and acetone have approximately the same solubility parameters,

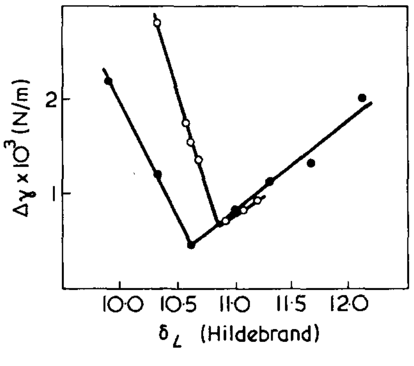

Figure 2 Differences (Δγ) between the surface tensions of solutions of *o*-hydroxypropyl cellulose and the surface tensions of the solvent mixtures as a function of the solubility parameter values of the solvent mixtures: ○, acetone/water mixtures; ●, DMF/THF mixtures

9.9 and 10.0 Hildebrands, the amount of solvent taken up by the surface layer of polymer would be similar and the 'surface tension' of the polymer would be reduced by a similar amount in both instances. A minimum would still be expected at the point where δ_p and δ_L have the same value.

The average experimental value for the solubility parameter of *o*-hydroxypropyl cellulose, in strong and moderate hydrogen bonding solvents, is 10.7 Hildebrands. The calculated value is 10.2 and the value in poor hydrogen bonding solvents would be expected to be less than 10.7. This is lower than might be anticipated for a water-soluble polymer. However a structure for the polymer has been proposed by Samuels[5] in which the hydroxyl groups of the anhydroglucose units and of the propylene glycol chains are predominantly intramolecularly hydrogen bonded. This would reduce the interchain forces of attraction and give a relatively low solubility parameter. The aqueous solubility and the extremely wide solubility spectrum in strong hydrogen bonding liquids is due to the numerous sites on the polymer chain available for bonding with these solvents. As the hydrogen bonding power of the solvents decreases the width of the solubility spectrum decreases. Thus it is the aqueous solubility, not the organosolubility, that must be regarded as anomalous. This agrees with the fact that *o*-hydroxypropyl cellulose is thermoplastic and can be readily melt processed[3], making it unique among water-soluble cellulose derivatives.

ACKNOWLEDGEMENT

The authors wish to thank Hercules Inc. for the sample of *o*-hydroxypropyl cellulose.

REFERENCES

1 Thomas, I. M. *BSc (Applied Chemistry) Dissertation* Trent Polytechnic, 1975
2 Gardon, J. L. 'Encyclopedia of Polymer Science and Technology' Wiley, New York, 1965, vol 3, p 833
3 Anon, 'Chemical and Physical Properties of 'Klucel', Hercules Inc., Wilmington, Delaware, 1968
4 Small, P. A. *J. Appl. Chem.* 1953, **3**, 71
5 Samuels, R. *J. Polym. Sci.* 1969, **7**, 1197
6 Burrell, H. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd Edn, Wiley–Interscience, New York, 1975, p IV-337

Effect of accelerator system and addition of lignin on the network structure of natural rubber vulcanizate

M. G. Kumaran, Rabindra Mukhopadhyay and Sadhan K. De
Rubber Technology Laboratory, Department of Chemistry, Indian Institute of Technology, Kharagpur–721302, India

(Received 15 September 1977)

Kumaran and De[1–3] showed that lignosulphonate (hereafter referred to as lignin) lowered the tensile strength, modulus, hardness and resilience and increased the abrasion resistance and flex resistance of natural rubber vulcanizates. While studying different accelerator systems in lignin-containing vulcanizate[3] it was observed that increase in compression set[4] due to addition of lignin was less in the MBT system than that in other systems (CBS/CBS–TMTD/CBS–DPG/MBT–DPG). In order to understand the possible correlation between the vulcanizate structure and properties of the vulcanizates, we have studied the effect of different accelerator systems on the vulcanizate network structure in the absence and in the presence of lignin.

EXPERIMENTAL

Details of materials, mixing, vulcanization and testing procedures have been published earlier[1–3,5]. The compositions of the mixes used in the present study are shown in *Table 1*. Vulcanizates were prepared by curing the compounded stock at 140°C for the respective optimum cure times, determined by using a viscurometer[3]. The $\bar{M}_n$ values of the rubber in the mixes were in the range of 1.4×10^5 to 1.5×10^5, as determined by the determination of the limiting viscosity number[5,6]. Chemical crosslink density was determined by the swelling method[5,7–10] and the crosslink type (mono-, di-, polysulphidic) by using thiol–amine chemical probes[11,12]. The total sulphur was determined by the combustion of the vulcanizate, followed by absorption of the sulphur dioxide in hydrogen peroxide and quantitative titration of the resulting sulphate ions[9]. Sulphide sulphur was determined iodometrically from the formation of cadmium sulphide[14]. F values were calculated as the number of g ions of sulphide sulphur present in the network per chemical crosslink[18].

The crosslink efficiencies, E and E' were calculated as the number of atoms of sulphur combined in the vulcanizate network per chemical crosslink before and after treatment with triphenyl phosphine[9]. The E value is interpreted as a measure of overall structural complexity of a sulphur vulcanized network, while E' is a direct measure of sulphur combined in the main chain modification such as cyclic sulphidic groups and pendant sulphidic groups.

Table 1 Composition of the mixes

Mix No.	1	1A	2	2A	3	3A	4	4A
Natural rubber	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3
N-cyclohexyl-2-benzothiazyl sulphenamide (CBS)	0.6	0.6	0.6	0.6	–	–	–	–
Diphenyl guanidine (DPG)	0.1	0.1	–	–	0.2	0.2	–	–
Tetramethyl thiuram disulphide (TMTD)	–	–	0.1	0.1	–	–	–	–
Mercapto benzothiazole (MBT)	–	–	–	–	0.8	0.8	1.0	1.0
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Lignin	0	10	0	10	0	10	0	10