

CHANGES TO THE PROPERTIES OF A POLYMER BY SOLVENT UPTAKE MEASURABLE AS CHANGES IN OXIDATION REACTIVITY

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1. INTRODUCTION

Solvent uptake by a non-porous solid is thermodynamically analogous to the mixing of two liquids, the mechanism being imbibition of the liquid by the solid. If two flammable liquids were mixed one would expect the resulting blend to have a different combustion reactivity to that of either of the constituents. Similarly, according to the reasoning in the first sentence of this paragraph, if a liquid is imbibed by a solid one might expect that the solid so treated would have a different reactivity towards combustion than before solvent imbibition. This hypothesis has been examined by the present authors and the work is ongoing. Some preliminary results are described herein not only because they are sufficiently novel to merit reporting in advance of a detailed coverage but also to stimulate discussion.

2. EXPERIMENTAL

The instrument used was a Thermometric 2277 Thermal Activity Monitor. A sample for testing was placed in a steel ampoule. The instrument had previously been stabilised at the desired temperature overnight. The ampoule containing the sample was then placed in the equilibration position. The reference ampoule, containing air only, was also placed in its equilibration position. Thermal equilibration of the samples took place over a one-hour period. The ampoules were then lowered into the measuring position and the signal followed at a potentiometric recorder connected to the instrument. The ampoules were left in the measuring position for several hours. When the final heat release reading at the recorder was taken it was checked against that on the digital display on the microcalorimeter. The instrument was recalibrated at each change of temperature setting.

The polymer was tested for heat-release rate at a particular temperature, after which the ampoule was removed from the instrument, the ampoule opened up and roughly 2 cm³ of kerosene added. The ampoule was then shaken mechanically for an hour and the heat-release rate of the treated polymer measured. Any kerosene not having been taken up was decanted from the ampoule. Note

however that any remaining could not have affected the results. No residual liquid or vapour will give a signal at the instrument: this point has been made by the present group several times previously [e.g. 1].

Heat-release rates for the polymer with and without the imbibed kerosene were determined at five temperatures (see results) for five samples of the polymer.

3. MATERIALS

The polymer used was neoprene, supplied as a sheet by Rubberatkins, Aberdeen.

4. RESULTS AND DISCUSSION

These are shown purely in tabular form in Table 1. These numerical data represent about 30 days of instrument time. With a reasonable degree of reproducibility, certainly freedom from behaviour at all erratic, the kerosene reduces the heat-release rate of the neoprene, by about 10% at 60°C, by about 20% at 70°C, by about 20% at 75°C, by about 26% at 80°C and by about 20% at 85°C. The results plotted in Arrhenius fashion for the polymer with and without the kerosene have been examined and show reasonable conformity. However, the most satisfactory way of discussing these findings is not by conventional kinetic approaches but to continue the theme of discussion along the lines introduced earlier. Relevant factors are:

- The compatibilities in mixing terms of the polymer and the solvent
- The respective reactivities of the two to oxygen

The first of these affects the extent of imbibition which of course affects the composition of any kerosene-treated sample, and is temperature dependent. Across the temperature range of the experiments the compositions of the neoprene/kerosene composite will have varied and the result measured at the microcalorimeter is the heat-release rate at the set temperature of a

composite of unknown proportions. This is why conventional Arrhenius analysis is not deemed appropriate. In this work there is the further

complication that the ‘solvent’ is itself a blend, not a pure hydrocarbon liquid.

Table 1: Microcalorimetric results

Instrument Temperature 60 °C



Amount of neoprene/mg	Rate of heat release/ μW		Amount of heat released W kg^{-1}		Change due to the kerosene/ W kg^{-1}
	Before exposure to kerosene	After exposure to kerosene	Before exposure to kerosene	After exposure to kerosene	
760	18.0	14.5	0.0237	0.0191	- 0.0046
630	13.0	11.6	0.0206	0.0184	- 0.0022
1170	32.8	31	0.0280	0.0265	- 0.0015
910	25.6	23	0.0281	0.0253	- 0.0028
1000	24.6	22.8	0.0246	0.0228	- 0.0018
		<u>Mean</u>	0.0250	0.0224	- 0.0026

Instrument Temperature 70 °C



Amount of Neoprene	Rate of heat release/ μW		Amount of heat released W kg^{-1}		Change due to the kerosene/ W kg^{-1}
	Before exposure to kerosene	After exposure to kerosene	Before exposure to kerosene	After exposure to kerosene	
890	53	39	0.0596	0.0438	- 0.0158
840	50.3	39.5	0.0599	0.0470	- 0.0129
1310	88.3	79	0.0674	0.0603	- 0.0071
680	38.7	28.5	0.0569	0.0419	- 0.0150
570	30.9	26	0.0542	0.0456	- 0.0086
		Mean	0.0596	0.0477	-0.0119

Instrument Temperature 75 °C



Amount of Neoprene	Rate of heat release/ μW		Amount of heat released W kg^{-1}		Change due to the kerosene/ W kg^{-1}
	Before exposure to kerosene	After exposure to kerosene	Before exposure to kerosene	After exposure to kerosene	
560	42.6	28	0.0761	0.0500	- 0.0261
690	56.1	46.3	0.0813	0.0671	- 0.0142
760	60.3	49	0.0793	0.0645	- 0.0148
860	69.1	57.1	0.0803	0.0664	- 0.0139
1040	85.3	72.6	0.0820	0.0698	- 0.0122
		Mean	0.0798	0.0636	- 0.0162

Instrument Temperature 80 °C

Amount of Neoprene	Rate of heat release/ μW		Amount of heat released W kg^{-1}		Change due to the kerosene/ W kg^{-1}
	Before exposure to kerosene	After exposure to kerosene	Before exposure to kerosene	After exposure to kerosene	
930	117.2	95	0.1260	0.1022	- 0.0238
580	68.5	51.3	0.1181	0.0884	- 0.0297
780	112	81.5	0.1436	0.1045	- 0.0391
1210	203.7	149.7	0.1683	0.1237	- 0.0446
730	98.1	68.5	0.1344	0.0938	- 0.0406
		<u>Mean</u>	0.1381	0.1025	- 0.0356

Instrument Temperature 85 °C

Amount of Neoprene	Rate of heat release/ μW		Amount of heat released W kg^{-1}		Change due to the kerosene/ W kg^{-1}
	Before exposure to kerosene	After exposure to kerosene	Before exposure to kerosene	After exposure to kerosene	
590	90.1	66.5	0.1527	0.1127	- 0.0400
630	104.3	83.7	0.1656	0.1329	- 0.0283
750	126	103	0.1680	0.1373	- 0.0307
970	163.4	152.7	0.1685	0.1574	- 0.0111
1140	209.1	182	0.1834	0.1596	- 0.0238
		<u>Mean</u>	0.1676	0.1400	- 0.027

5. CONCLUDING REMARKS

The findings then are that kerosene does deactivate neoprene in a way which has a strong positive dependence on temperature. That it should either activate it or deactivate it on imbibition is expected. When two petroleum fractions are mixed the reactivity (taking care not to confuse reactivity with volatility, a fairly common error) of the blend will differ from that of either constituent and, as pointed out earlier, the physical chemistry of solvent uptake by a polymer can be treated similarly to the mixing of two liquids.

REFERENCES

1. J.C. Jones, "The activation to combustion of a previously inert material by solvent imbibition", *Journal of Fire Sciences*, Vol. 21 pp. 339-342 (2003).