

# Adhesive Behavior of the Two Phase System: Polyisobutylene–Sodium Carboxymethylcellulose

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## Synopsis

Adhesive properties of polyisobutylene filled with sodium carboxymethylcellulose have been studied. From the results obtained by the removing cylinders method the lifetimes of the cylinder–PIB/CMC composition joint were calculated. The compositional dependence of the lifetimes have a similar character to that representing the dependence of relaxation time on the composition.

## INTRODUCTION

Polyisobutylene (PIB) is widely used in the rubber manufacturing and adhesive industries. A particularly important application of the low-molecular-weight PIB is in the pressure-sensitive adhesive (PSA) formulations. It has become well established that the adhesion behavior of elastomeric compositions strongly depends on their viscoelastic properties.<sup>1–4</sup> Thus, the possibility of separating the quantitative contributions to the adhesive strength from the rheological losses and the interfacial bonding have been demonstrated.

According to Andrews and Kinloch<sup>7</sup> the adhesive failure energy  $\theta$  is given by

$$\theta = \theta_0 f(R) \quad (1)$$

where  $\theta_0$  is the intrinsic adhesive failure energy which depends only on the physical and chemical structure of the adhesive–substrate interface, and  $f$  is a function of the reduced rate of failure propagation.  $\theta_0$  corresponds to the work of bond fracture across the interface and, for a clean interfacial failure, is equal to the thermodynamic work of adhesion,  $W_A$ . When the failure is not purely interfacial,  $\theta_0$  can be expressed as

$$\theta_0 = iI + rT + sF \quad (2)$$

where  $i$ ,  $r$ , and  $s$  are the area fractions of the interfacial, cohesive-in-rubber, and cohesive-in-substrate failure, respectively, and  $I$ ,  $T$ , and  $F$  are the intrinsic failure energies for the interface, rubber, and substrate, respectively.

More recently, Aubrey and Ginostatis<sup>5</sup> have focused their attention on the contributions to the adhesive strength arising from interfacial effects and from another effect related to changes in the viscoelastic state of the

adhesive bulk. It has been found that the latter effect contributes most significantly to the increased peel force at a given peeling rate.

In the present work, the adhesive properties of PIB filled with sodium carboxymethylcellulose (CMC) have been studied. Such a composition is widely used as a main component of PSAs suitable for contact with human body, since apart from the excellent adhesion and physiological neutrality it is capable of absorbing moisture. In this two-phase system, the filler significantly affects rheological properties,<sup>6</sup> thus influencing also the adhesion.

## EXPERIMENTAL

Polyisobutylene Oppanol B 15 (BASF) of molecular weight  $\bar{M}_v = 85 \times 10^3$  and sodium carboxymethylcellulose Blanose 7HXF (Hercules, United Kingdom) were used. The PIB/CMC compositions differing in the CMC content were prepared on rollers at 383 K. The time of rolling was 10 min. The samples are coded with the symbol PIB/CMC followed by a numerical index indicating the weight ratio of the components, e.g., 100/0, 80/20, etc. The rheological characteristics of the PIB/CMC compositions are described in detail elsewhere.<sup>6</sup>

In order to assess the adhesive properties the following methods were used.

**The Band Stripping Method (Peeling Test).** The PIB/CMC compositions were pressed between two sheets of poly(ethylene terephthalate) for 5 min applying the pressure of 30 MPa. The thickness of the adhesive layer was ca. 0.2 mm. Strips 10 cm long and 1 cm wide were cut off from the laminate. Lose ends of the polyester film were mounted into the clamps of an Instron (United Kingdom) machine and pulled apart at the rate 1, 10, 100, and 500 mm/min.

**The Cylinder Removal Method.** Films, of the PIB/CMC compositions, approximately 1 mm thick, were compression molded between a metal substrate and a silicone-coated release paper. The substrate was then mounted horizontally in the Instron machine, the release paper removed, and a cylinder lowered down at the rate 10 mm/min to contact the adhesive surface. Cylinders made of steel, poly(methyl methacrylate) (PMMA) and polytetrafluoroethylene (PTFE) all having the base surface area 1 cm<sup>2</sup> and mass 11.5 g were used. Each cylinder remained in contact with the adhesive surface for 60 s before it was removed at the rate 1, 10, 50, 100, or 500 mm/min. The force required was recorded.

## RESULTS AND DISCUSSION

The results presented in Table I show the dependence of the peel force (here equal to the energy per surface area) on the pulling rate, at room temperature. Visual examinations of the surface recovered by peeling polyester film indicate that the character of separation clearly depends on the pulling rate. At the small pulling rates, the separation occurs in the bulk of the adhesive, i.e., the separation is cohesive. Much filamentation of the adhesive is noticed during the separation, and it is clear that the viscous flow plays an important role in this region. One should expect that increase

TABLE I  
The Results of the Peeling Test

$\delta$ (N/cm)	Elongation rate $V$ (mm/min)				$\delta = k \cdot V^\alpha$	
	1	10	100	500	$k$	$\alpha$
Composition						
100/0	0.27	0.98	3.3	7.3	0.28	0.53
95/5	0.25	1.0	3.4	7.7	0.26	0.55
90/10	0.20	0.61	3.2	8.9	0.18	0.62
85/15	0.15	0.49	3.3	9.3	0.13	0.68
80/20	0.15	0.58	3.4	8.6	0.14	0.66
70/30	0.14	0.35	3.0	7.5	0.11	0.67
65/35	0.11	0.20	2.5	6.3	0.08	0.70
60/40	0.14	0.39	2.7	4.3	0.13	0.58
50/50	0.21	0.34	2.0	—	0.17	0.55

in the adhesive viscosity causes an increase of the peeling force. Nonetheless, the actual situation has been found reversed. One should remember, however, that cohesive integrity of the two-phase PIB/CMC system is lowered by the presence of the inert, inactive CMC component. This factor dominates over the effect of the viscosity increase, and therefore a decrease of the tearing force with increasing CMC content is observed.

An increase in the pulling rate brings about changes in the character of the separation of polyester films. At the high rates, there is no apparent filamentation and the adhesive surface remains smooth and glassy. The separation occurs at the adhesive/polyester interface. Besides, at the high pulling rates, no significant effect of the CMC content on the peeling force is observed. The surface produced by peeling have similar appearance. Independently of the CMC content, the adhesive layers recovered seem to be composed of pure PIB, making the surface tensions of all compositions similar. Nevertheless, it is not the equality of the surface energetic characteristics that is responsible for the similar values of the peel forces. The fracture energy per unit area of the fracture surface is given by the thermodynamic or reversible work of adhesion,  $W_A$ , and the energy,  $W_D$ , dissipated in the irreversible process of crack formation. In the case of reversible separation, the  $W_D$  term can be neglected. On the other hand, at the high rates of separation,  $W_D$  is usually much larger than  $W_A$ . This is also the case in the present measurements at the high pulling rates. Therefore, it should be concluded that the viscoelastic response of all PSAs studied is nearly the same. Since we do not have at our disposal method of correlating the pulling rate with the shear rate, it is impossible, at present, to interpret the adhesive behavior of the PSAs studied in terms of their viscoelastic properties.

As it is seen in Figure 1, the relationship between the peel force ( $\delta$ ) and the pulling rate ( $v$ ) can be described by

$$\delta = k \cdot V^\alpha \quad (3)$$

The values of  $k$  and  $\alpha$  are listed in Table I. The curves  $\delta$  vs.  $V$  intersect in

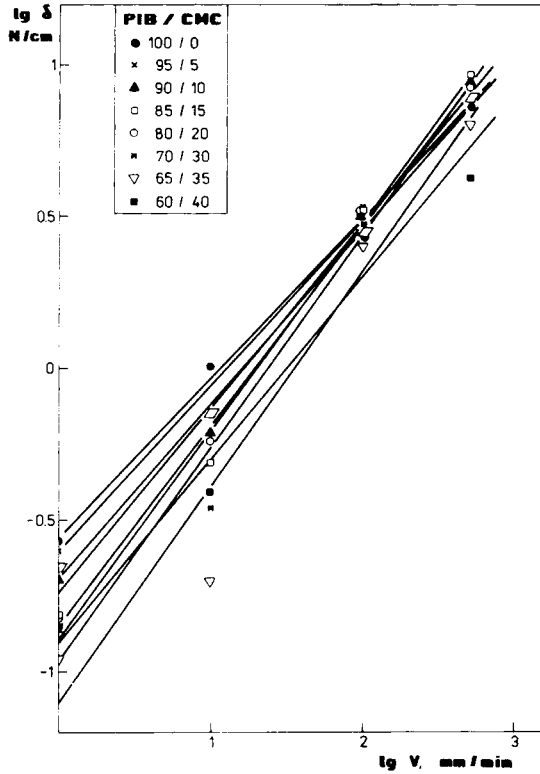


Fig. 1. Relationship between the peel force ( $\delta$ ) and the pulling rate  $V$ . PIB/CMC: (●) 100/0; (×) 95/5; (▲) 90/10; (□) 85/15; (○) 80/20; (\*) 70/30; (▽) 65/35; (■) 60/40.

a single point  $\log V = 2$ , corresponding to the pulling rate 100 mm/min (cf. Fig. 1).

The results of the assessment of the adhesive properties obtained by the method of removing cylinders from the PSAs surfaces are listed in Table II. A characteristic feature observed in this experiment is a maximum in the removing force vs. removing rate relationship. Up to the rate of 100 mm/min, the removing force increases with increasing rate, but at 500 mm/min the value of the removing force significantly decreases. In the range of rates 1–100 mm/min, the removing force vs. removing rate relationship has an exponential character, as in the peeling test. It is therefore possible to calculate the lifetime of the cylinder-PIB/CMC composition joint.

If a sample is subjected to subsequent stresses  $\sigma_i$  to which correspond a lifetime  $\tau$ , and the duration of each stress is  $dt$ , the break occurs when the following condition is fulfilled<sup>7</sup>:

$$\int_0^{\tau} \frac{dt}{\tau[\sigma(t)]} = 1 \quad (4)$$

TABLE II  
The Force of Removal Cylinders from PIB/CMC Surfaces

Composition PIB/CMC	Pulling rate (mm/min)	Contact surface		
		Steel	PMMA	PTFE
100/0	1	7.2	8.6	5.2
	10	18.6	20.0	14.9
	50	27.8	30.8	20.7
	100	32.3	34.9	23.8
	500	20.2	33.4	16.0
95/5	1	6.8	7.3	6.0
	10	15.0	16.7	10.9
	50	20.5	20.0	19.0
	100	22.4	24.5	22.7
	500	16.1	24.0	15.3
90/10	1	7.7	6.9	7.1
	10	15.8	14.8	12.1
	50	23.5	24.9	19.7
	100	27.4	28.6	22.9
	500	17.1	15.4	18.9
85/15	1	7.2	7.0	6.3
	10	14.1	18.6	13.2
	50	19.2	26.0	18.0
	100	21.6	29.5	20.4
	500	15.2	21.5	14.2
80/20	1	9.9	8.1	6.2
	10	16.7	15.6	12.7
	50	18.0	25.0	15.5
	100	19.1	30.5	17.0
	500	15.8	21.0	14.4
70/30	1	6.3	6.9	6.1
	10	12.5	18.4	13.7
	50	14.5	27.3	15.5
	100	15.6	31.7	17.0
	500	12.6	23.6	12.6
65/35	1	8.0	10.0	6.3
	10	9.6	16.1	13.0
	50	15.4	26.0	14.2
	100	17.1	29.0	14.8
	500	10.9	18.8	8.5
60/40	1	4.7	7.5	4.8
	10	8.7	16.3	7.9
	50	10.7	24.0	11.1
	100	12.8	28.8	12.9
	500	13.8	26.0	7.6
50/50	1	3.2	3.2	1.2
	10	4.4	4.1	3.0
	50	6.5	7.2	4.4
	100	9.5	12.2	4.7
	500	2.6	7.6	3.6

Žurkov<sup>8</sup> has found the following relationship to exist between the lifetime and the stress:

$$\tau = Ae^{-\alpha\sigma} \quad (5)$$

where  $A$  and  $\alpha$  are the constants dependent on the kind of material. For a linear dependence of the stress in a sample and the rate of stress increase,  $W$ ,  $\sigma = W \cdot t$ , eq. (4) can be rewritten to read

$$\int_0^{\tau} \frac{dt}{Ae^{-\alpha Wt}} = 1 \quad (6)$$

Integration of (6) yields

$$e^{\alpha W\tau} - 1 = A\alpha W \quad (7)$$

or according to (5)

$$\frac{1}{\tau} - \frac{1}{A} = \alpha W \quad (8)$$

Since in most cases<sup>9</sup>  $\tau \ll A$ , then

$$\frac{1}{\tau} \cong \alpha W \quad (9)$$

Thus, the lifetime is inversely proportional to the rate  $W$ . Taking the logarithm of (9) and making use of (5), one gets<sup>9</sup>

$$\sigma = \frac{\ln(A\alpha)}{\alpha} + \frac{1}{\alpha} \ln W \quad (10)$$

which provides the relation linking the strength at a constant stress with the strength at a constant increase of stress. The kinetic concept of the strength of materials has been found to be useful not only with respect to homogeneous materials. It also describes well the behavior of the adhesive joints among immiscible polymers.<sup>10</sup> This concept is applied here to characterize the PSAs studied.

The lifetimes of the joints PIB/CMC composition-cylinder, under the stress 1 N/cm<sup>2</sup> are listed in Table III. Only for the mixture PIB/CMC (80/20) in contact with steel, was the result found unreasonably large (above 200 s), probably due to an error in  $\alpha$  value. This result is incomparable with the values obtained for the remaining samples.

The lifetimes for different cylinders do not indicate a presence of any effect of the kind of material. Since very small rates of removal correspond to the stress 1 N/cm<sup>2</sup>, one should expect a considerable effect of the reversible work of adhesion (the differences in surface tensions of PMMA,

TABLE III  
The Lifetimes of Adhesive Joints and Selected Rheological Parameters<sup>6</sup> of the PIB/CMC Compositions

Composition PIB/CMC	Lifetime (s) contact surface			Rheological properties of adhesive bulk		
	Steel	PMMA	PTFE	$\lambda$ (s)	$\psi_0 \times 10^{-6}$ (Pa s <sup>2</sup> )	$G_0 \times 10^{-5}$ (Pa)
100/0	16.03	19.69	11.85	3.21	16.47	5.33
95/5	19.88	21.94	10.34	2.37	11.73	6.96
90/10	17.79	15.70	15.59	1.59	7.25	9.56
85/15	22.28	16.83	17.00	3.85	10.03	6.75
80/20	—	16.20	26.00	5.61	46.28	4.90
70/30	33.67	15.37	26.22	11.49	186.48	4.71
65/35	39.40	27.27	46.00	27.84	576.29	2.48
60/40	16.67	16.50	12.57	9.22	149.09	5.85
50/50	4.39	3.13	1.00	1.52	25.08	36.2

PTFE, and steel are rather large). Nevertheless, the joint breaking has been found not to be purely adhesive. The separation occurs partly in the bulk of PSAs and their rheological properties have the decisive influence. A comparison of the relaxation times and elasticity moduli with the lifetimes confirms this conclusion. As can be seen in Figure 2, the curve illustrating

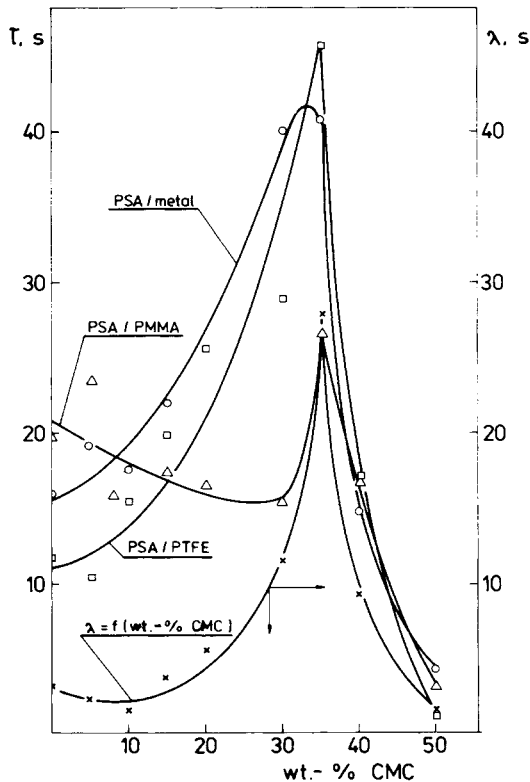


Fig. 2. Concentration dependence of life time ( $\tau$ ) and relaxation time ( $\lambda$ ).

the dependence of the relaxation time on the composition have a character similar to that representing the compositional dependence of the lifetimes. In all cases a maximum occurs at 35% of CMC content. At the same CMC content the lowest value of the elasticity modulus,  $G_0$ , and the highest value of the normal stress coefficient,  $\psi_0$ , occurs.

Thus, also in the case of specific PSAs such as PIB modified with CMC, the dependence of the adhesive behavior on the rheological properties of an adhesive itself has been confirmed, although, at the present stage, only qualitatively. There are a number of similarities as well as differences in the behavior of the PSAs studied with that of other compositions of this kind.<sup>5-11</sup> The dependence of the peel force on the pulling rate is for PIB/CMC compositions similar to that described by Aubrey and Ginosatis,<sup>5</sup> although no "slip-stick" region at high rate nor a region at which the peel force rapidly drops down and becomes rate-independent have been observed. The behavior of the PIB/CMC compositions corresponds even better to that described by Gardon<sup>11</sup> for acrylate-coated cellophane films where, at high pulling rates, a constant, high peel strength occurred.

The differences in the behavior of the present objects of studies compared with that of other compositions is partly due to different conditions at which the tests have been made.

The peeling tests in the works quoted were performed using a stiff glass substrate, while in the present work the substrate—polyester film—was flexible. Besides, the range of pulling rates at which the changes of separation character occur may also change and, depending on the test conditions, may fall beyond the range available.

## CONCLUSIONS

The effect of carboxymethylcellulose on adhesive properties of CMC/PIB was evaluated. The maximum of the peel force was observed in the region of 35 wt % of CMC. There exists correlation between adhesive behavior and rheological properties of these systems.

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