4

Polyisobutene-Based Pressure-Sensitive Adhesives

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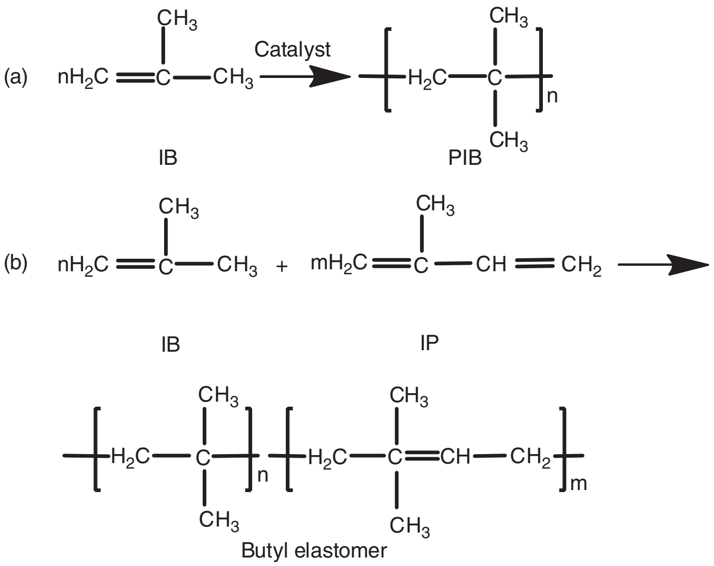
4.1 Polyisobutene (PIB): General Properties and Applications

PIB is a vinyl polymer that is made from the monomer isobutylene (IB) by cationic polymerization (Scheme 4.1a).

Despite its linear structure, PIB is usually classified as a synthetic rubber or elastomer. PIB has unique properties: very low air, moisture, and gas permeability, good thermal and oxidative stability, chemical resistance, and high tack in adhesive formulations. PIB is a colorless to light-yellow, elastic, semisolid or viscous substance. It is odorless, tasteless, and nontoxic. Because of their highly paraffinic and nonpolar nature, PIBs are soluble in aliphatic and aromatic hydrocarbon solvents and insoluble in polar solvents. Solubility generally decreases with increasing molecular weight of the polymer and increasing size of the aliphatic portion of the solvent molecule. The amorphous characteristics and low glass transition temperature ($T_g = -62°C$) of PIB impart high flexibility and permanent tack. Despite the favorable tack property, the adhesion of PIBs to many surfaces is weak because of their low polarity. This problem can be overcome by the addition of tackifiers (such as rosin ester resins) and other materials that will impart some polar properties to the formulation (see also Chapter 8). PIB is used in making



SCHEME 4.1 Polymerization of isobutylene (IB) to form polyisobutylene (PIB) (a); copolimerization with isoprene (IP) to form butyl elastomer (b).

TABLE 4.1 Physical Properties of PIB That are Independent of Molecular Weight

Density at 20°C	0.92 g/cm
Glass transition temperature, T_g (differential scanning calorimetry)	−62°C
Specific heat, *c*	2 $kJ \cdot kg^{-1} \cdot K^{-1}$
Thermal coefficient of cubic expansion at 23°C	6.3×10^{-4} K^{-1}
Thermal conductivity, *k*	0.19 $W \cdot K^{-1} \cdot m^{-1}$
Refractive index, $n^{20}D$	1.51
Dielectric constant, ε_r (50 Hz, 23°C)	2.2
Dissipation factor, *tg* δ (50 Hz, 23°C)	$\leq 5 \times 10^{-4}$
Specific resistance	1.016 Ω·cm
Coefficient of permeability to water vapor	2.5×10^{-7} $g \cdot m^{-1} \cdot h^{-1} \cdot mbar^{-1}$

adhesives, agricultural chemicals, fiber optic compounds, caulks and sealants, cling film, electrical fluids, lubricants (two-cycle engine oil), paper and pulp, personal care products, and pigment concentrates, for rubber and polymer modification, as a gasoline/diesel fuel additive, and even in chewing gum. Low- and medium-molecular-weight PIBs are used as viscosity modifiers, fuel and lubricating oil additives, tack improvers in adhesive formulations, and primary binders in caulking and sealing compounds. The most important physical properties of PIB are presented in Table 4.1.

PIBs are usually classified into two groups according to molecular weight. High-molecular-weight PIBs have a weight average molecular weight, M_w, of from 500,000 to 1,100,000 g/mol, preferably between 650,000 and 850,000 g/mol. Such polymers are available commercially, for example, under the trade name Oppanol® B80-B200, B30 SF–B50 SF (BASF AG, Ludwigshafen, Germany) or Vistanex® MM-L80 through L-140 (ExxonMobil Chemical Company, Houston, TX) [1–3].

Low- and medium-molecular-weight PIBs have a weight average molecular weight, M_w, of from 40,000 to 120,000 g/mol, preferably between 60,000 and 100,000 g/mol. Such polymers are available commercially, for example, under the trade name Oppanol B10 SFN-B15 SFN (BASF AG) or Vistanex LM-MH, LM-MS, and LM-H (ExxonMobil Chemical Company) [3,4].

The discovery of the low permeability of PIB led to the development of butyl rubber (BR). Butyl elastomer is a random copolymer of IB and 1–4 mol % of isoprene (IP) (Scheme 4.1b). Double bonds introduced into the macromolecule by isoprene permit the polymer to be cross-linked or vulcanized. The physical properties of BR are mostly the same as those of PIB: low permeability, good chemical and thermal stability due to the low unsaturation content, and high damping. BR is cross-linked (cured or vulcanized) with sulfur-based chemistry and mostly used as an inner liner or tube in tires to prevent air leakage. Other applications include tank liners, vibration dampers, protective clothing, tire curing bladders, railway pads, wire and cable coating, belting, and hoses. Cross-linked BR is also used for pharmaceutical stoppers and blood bags because of its excellent barrier properties. Both PIB and non-cross-linked butyl elastomers are approved by the Food and Drug Administration as a chewing-gum base and for other food-related applications (see also *Applications of Pressure-Sensitive Products*, Chapter 7). BR is used for PSAs as well (see Chapter 8).

BRs are available both in nonhalogenated and in several halogenated grades. A low-molecular-weight, semiliquid analog of BR is also available under the trademark Kalene® (Hardmann, Inc., Belleville, NJ). Kalene liquid BRs impart the performance benefits of BR and provide the processing convenience of a liquid. Kalene's butyl properties impart chemical resistance to a wide variety of sealants and adhesives. Kalene products provide tack to PSAs and they improve the adhesion of butyl-based adhesives and sealants. They also act as reactive plasticizers for conventional butyl to improve their compounding efficiency.

The halogenation of BR, with either chlorine or bromine, significantly increases cure reactivity, provides compatibility with unsaturated polymers, and enhances adhesion compared with regular BR. Significant improvements in heat, ozone, flex fatigue resistance, and compression set can be achieved through the selection of appropriate compounding ingredients and curing systems. Chloro-BR is prepared by chlorinating the regular butyl polymer under controlled conditions so that the reaction is primarily by substitution and little of the unsaturation originally present in the macromolecules is lost. ChloroBR consists of approximately 1.2 wt % chlorine, which tends to enhance the reactivity of the double bonds as well as supply additional reactive sites for cross-linking. Brominated butyl polymers are also available. They are similar to chlorobutyl, but provide an additional level of cross-linking activity. Bromo-BR consists of approximately 20 wt % bromine.

A relatively new family of butyl elastomers are star-branched (SB) butyl polymers, both nonhalogenated and halogenated. These polymers have a unique molecular weight distribution due to incorporating large SB molecules with butyl arms. SB butyl polymers have

TABLE 4.2 Commercial Grades of PIBs

Name	Grade	Viscosity Average Molecular Weight (M_v/g/mol)	Comments
BASF Oppanol B	10 SNF	40,000	Soft, resin-like polymers, used in the production of adhesives, sealants, lubricants, coatings, and chewing gum
	11 SNF	49,000	
	12 SNF	55,000	
	13 SNF	65,000	
	15 SNF	85,000	
	30 SF	200,000	Soft, resin-like polymers, used for producing adhesives, sealants, lubricating oils, coating compounds, and chewing gum; also recommended for modifying bitumen
	50/50 SF	400,000	
	80	800,000	
	100	1,100,000	Rubbery polymers, used for the production of adhesives, sealants, lubricants, and coating compounds
	150	2,600,000	
	200	4,000,000	
Exxon Vistanex	LM-MS	44,000	Semiliquid polymers, used mainly as permanent tackifiers in a variety of cements, PSAs, and hot-melt adhesives; useful for enchancing adhesion to polyolefin surfaces
	LM-MH	53,000	
	LM-H	63,000	
	MM L-80	900,000	Rubber-like solids used to impart strength and flow resistance to solvent cement and PSA label stock; also used in certain hot-melt adhesion compositions where they provide flexibility and impact resistance, particularly at low temperature
	MM L-100	1,250,000	
	MM L-120	1,660,000	
	MM L-140	2,110,000	
Kalene liquid BR	800	36,000	Used as bases for sealants, coatings, and adhesives
	1300	42,000	
Exxon butyl	007	450,000	Used in products needing low permeability to gases and liquids, e.g., tire inner liners, hoses, seals of certain types, and membranes; also suitable for curing bags, pharmaceutical stoppers, and rubber articles needing good resistance to chemicals, weathering, and ozone, such as tank linings, conveyor belts, and protective clothing
	065	330,000	
	068	450,000	
	165	330,000	
	268	480,000	
	269	520,000	
	365	330,000	
Lanxess butyl	101-3		
	301		
	402		
Exxon chlorobutyl	1066	400.000	Chlorobutyl can be blended with both regular butyl and natural rubber and then preferentially cured through chlorine to improve strength; the reactive chlorine increases adhesion to many polar substrates
	1068	480.000	
Lanxess chlorobutyl	1240		
Exxon bromobutyl	2211		Used for the production of tires, particularly tire inner liners and tire sidewalls, and for pharmaceutical rubber articles
	2222	330,000	
	2235	420,000	
	2244	450,000	
	2255	450,000	

(*continued*)

TABLE 4.2 (Continued)

Name	Grade	Viscosity Average Molecular Weight (M_v/g/mol)	Comments
Lanxess bromobutyl	2030 2040 X2		
Exxon SB butyl	4266 4268	All grades are bimodal and contain approximately 13–14 wt % high-molecular weight star fraction	Used in pharmaceutical closures, etc.
Exxon SB chlorobutyl	5066		
Exxon SB bromobutyl	6222 6255		
Exxpro speciality elastomer	3035 3433 3745	430,000 350,000	Used when extended age resistance at high temperature is needed
Lord BR latex	BL-100		Used in packaging adhesive applications and as a tackifying and flexibilizing additive in higher strength adhesives based on more brittle polymers

functional properties of butyl and halobutyl polymers. However, because of their unique molecular weight distribution, they offer improvements in green strength (uncured strength)/stress relaxation balance and melt rheology. This leads to potential benefits in reduced cold flow, better extrudate/calendered surface quality, and enhanced mixing.

Exxpro elastomers are new elastomers that are randomly brominated copolymers of *para*-methylstyrene (PMS) and isobutylene with varying degrees of PMS content and bromination on the *para*-methyl group. These elastomers retain all the properties of butyl and halobutyl, but the inertness of the backbone improves heat, ozone, and flex resistance.

BR can be also emulsified to give a latex. The advantage of latex is high (approximately 60 wt %) solid content and low viscosity. Butyl latex has excellent mechanical, chemical, and freeze–thaw stability, which allows compounding and blending with other ingredients. When dried, it possesses the typical butyl characteristics of low aging, flexibility, low permeability, and tack.

Commercial grades of PIBs and BRs are listed in Table 4.2.

4.2 Polyisobutene-Based Pressure-Sensitive Adhesives

PIB has long been used as a basic substance in the compounding of pressure-sensitive adhesives (PSAs). Relative to other known elastomers, synthetic polymers based on isobutylene offer a number of advantages. Owing to their synthetic production, they are free of unwanted ingredients and due to their complete saturation they are highly stable to oxidation. PIBs are not a skin irritant and adhesives used in medicine (e.g., surgical tape adhesive, transdermal systems) [5] are usually based on PIBs (see also *Applications of Pressure-Sensitive Products*, Chapter 4).

PIBs are used in many adhesive formulations due to their tackiness, flexibility, and low cohesive strength, mainly in PSAs and hot-melt adhesives.

PSAs for removable labels and tapes are usually formulated as blends of rubber and tackifying resins (see also Chapter 8). High-molecular-weight PIBs are strong and elastic and can serve as the elastomeric base of PSAs [1,2]. Low-molecular-weight PIBs are very soft and liquid-like, making them suitable tackifiers [4]. Tack and holding power are two important parameters for PSAs (see also *Fundamentals of Pressure Sensitivity*, Chapters 6 and 8, and *Applications of Pressure-Sensitive Products*, Chapter 7). Tack of PIB-based PSAs can also be adjusted with different resins and other tackifiers. The cohesive strength of PIBs is relatively low, but can be increased by the addition of high-molecular-weight PIB or fillers. PSAs formulated with PIB are aging-resistant and used for adhesion to a variety of substrates [e.g., glass, metal, paper, polyvinyl chloride (PVC) and polyester films].

PIBs can also be formulated in hot-melt PSA (HMPSA) recipes. PIBs improve the flexibility of the system, provide good aging and chemical resistance, and increase tack. However, high-molecular-weight grades of PIB increase melt viscosity and, therefore, they are usually blended with a significant amount of tackifying resin, petrolatum, or amorphous polypropylene to reduce viscosity to an appropriate level.

It should also be noted that PIB-based PSAs are widely used in the medical field [5,6], especially for transdermal drug delivery (TDD) systems [7–12] (see also *Applications of Pressure-Sensitive Products*, Chapter 4). TDD systems are drug-loaded adhesive patches that, when applied to the skin, deliver the therapeutic agent, at a controlled rate, through the skin to the systemic circulation and the target organs [9]. In TDD applications, adhesives are used to maintain intimate contact between the patch and the skin surface. The manufacturers of PIB polymers do not supply preformulated, ready-to-use adhesives; therefore, the TDD patch manufacturers or formulators usually compound their own PIB–PSA recipes.

There are three common approaches to obtain desired PSA properties. First, a combination of low- and high-molecular-weight PIBs is used to achieve a balance of tack and cohesive strength. Such adhesives can be easily manufactured by solution or dry blending and a certain ratio of low- to high-molecular-weight PIB is required for pressure-sensitive adhesion. Conventionally, this is accepted to be about 80 wt % or less of low-molecular-weight PIB. This sort of formulation yields PSAs with fairly mild adhesive characteristics. Second, high- and medium-molecular-weight PIBs are blended with a low-molecular-weight polybutene (PB). When PB is added to the PIB mixture, the formulation range expands. One can use higher ratios of high- to low-molecular-weight PIB. The formulation then becomes a compromise between highly tacky material (high amount of PB) and materials with low shear strength. Third, tackifiers, plasticizers, fillers, waxes, oils, and other additives can be incorporated into the formulation to impart the desired adhesive properties and viscosity. Fully formulated PIB adhesives for TDD applications are available from Adhesives Research, Inc. (Glen Rock, PA) and custom formulations can be provided by other vendors such as Mactac (Moosic, PA) and National Starch and Chemical Company (Bridgewater, NJ) [9].

Several typical PSA formulations illustrating some of the application, as well as their suppliers, are listed in Table 4.3 and can also be found in handbooks and patent literature [13–23].

TABLE 4.3 PSA Formulations

Component	Supplier	Content
A. Pressure-Sensitive Adhesive [3]		
Vistanex PIB MM L-120	Exxon Chemical Co.	100 parts
Hercolyn	Hercules, Inc.	30 parts
Piccolyte S115	Hercules, Inc.	45 parts
Parapol 950	Exxon Chemical Co.	70 parts
B. BR HMPSA [13]		
Exxon butyl 065	Exxon Chemical Co.	100 parts
Ercorez 5320 resin	Exxon Chemical Co.	10 parts
Petrolatum		50 parts
Amber mirowax (Be Square 175)	Petrolite Corp., Polymer Div.	150 parts
Antioxidant (Ethanox 702 or Irganox 1010)	Albemarle Corp.	1 part
C. High Heat-Resistant PSA [13]		
Exxpro elastomer	Exxon Chemical Co.	100 parts
Ercorez 2550 resin	Exxon Chemical Co.	110 parts
Ercorez 5380 resin	Exxon Chemical Co.	15 parts
Cross-linker (e.g., triethylene tetramine)		0.5 parts
Antioxidant		2 parts
D. Monolith Adhesive Transdermal System [17]		
PIB Oppanol B1	BASF	5 g
PIB Oppanol B10	BASF	3 g
PIB Oppanol B100	BASF	9 g
Hydrogenated carbon resin Ercorez 5320	Exxon Chemical Co.	43 g
1-dodecylazacycloheptan-2-one	Azone, Nelson Res., Irvine, CA	20 g
Active ingredient (3-amino-1-hydroxypropane-1,1-diphosphonic acid)		20 g
E. Adhesive Material for Skin [15]		
Vistanex PIB LM-MH	Exxon Chemical Co.	41.5%
Kraton D1107 (Styrene–isoprene–styrene copolymer)		8.5%
Gelatine P.S.98.240.223	Ed. Geistlich Söhne AG	17.5%
Pectine LM12 CG Z or USP/100	Copenhagen Pectin A/S	10%
CMC (carboxylmethylcellulose) AF2881	Akzo	22.5%

4.3 Rheology, Viscoelasticity, and Adhesion of Polyisobutylene-Based Pressure-Sensitive Adhesives

PIB is a linear polymer with a moderate width of molecular weight distribution. Typically, the ratio of weight-to-number average molecular weight, M_w/M_n, is around 2. The rheological properties of such polymers are essentially controlled by M_w and temperature, T. Low-molecular-weight grades ($M_w < 10^4$ g/mol) exhibit newtonian flow behavior at room temperature and above and in this case the viscosity, η, is directly proportional to M_w.

Higher-molecular-weight PIBs are shear thinning and the dependence of viscosity, η, on shear rate, $\dot{\gamma}$, is well described by the Cross model [24].

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1+|\lambda\dot{\gamma}|^{0.75}} \tag{4.1}$$

Here, λ is a characteristic time constant depending on molecular weight and temperature (and pressure), whereas η_0 is the viscosity in the limit of low shear rates, the so-called zero-shear viscosity. The molecular weight dependence of this important quantity has been investigated intensively [25–28]. The following relationship between η_0 and M_w has been extracted from a large set of experimental data [28].

$$\eta_0 = 4.69 \cdot 10^{-12} \cdot M_w^{3.43} \cdot Pa \cdot s \tag{4.2}$$

This relation is valid for $T = 25°C$. The temperature dependence of η_0 is described by the William–Landel–Ferry (WLF) equation and can be expressed in terms of a shift factor a_T,

$$\log a_T = \log\left(\frac{\eta_0(T)}{\eta_0(T_0)}\right) = -\frac{c_1(T-T_0)}{c_2+(T-T_0)} \tag{4.3}$$

with $T_0 = 25°C$, $c_1 = 8.61$, and $c_2 = 200$ K [27], which is consistent with other literature data [28,29] referring to other reference temperatures, T_0.

At temperatures well above T_g, the WLF equation can also be approximated by an Arrhenius equation with a single activation energy parameter, E_a. The linear viscoelastic properties of polymers are usually described in terms of a complex frequency-dependent shear modulus $G^*(\omega) = G' + iG''$, where the storage modulus, G', characterizes the elastic and the loss modulus, G'', characterizes the viscous contribution to stress relaxation (see also *Technology of Pressure-Sensitive Adhesives and Products*, Chapter 5, *Fundamentals of Pressure Sensitivity*, Chapter 5, and *Applications of Pressure-Sensitive Products*, Chapter 7). A typical result for PIB (Oppanol B50, $M_v = 400{,}000$ g/mol) is illustrated in Figure 4.1. These G' and G'' curves demonstrated two characteristic crossover frequencies ($G' = G''$), ω_c and ω_e, which separate the spectra into three parts. At frequencies below ω_c, in the so-called flow regime or terminal zone, G'' dominates over G' and $G' \sim \omega^2$, whereas $G'' \sim \omega$. In the intermediate so-called entanglement or rubbery regime, $G' = G_0$ is essentially independent of frequency and $G' >> G''$. This is a consequence of the topological constraints the polymer chains impose on each other. This phenomenon is also called entanglement and the entanglements are like physical, nonpermanent cross-links, which control stress relaxation. The corresponding plateau modulus $G_0 = \rho RT/M_e$ is directly related to the average molecular weight between two entanglements, M_e. This constant is a material property independent of molecular weight and for PIB $M_e = 8{,}700$ g/mol [30]. In the glass transition zone both G' and G'' exhibit power-law behavior and finally, at high enough frequencies, the shear modulus G_s of the solid material is reached.

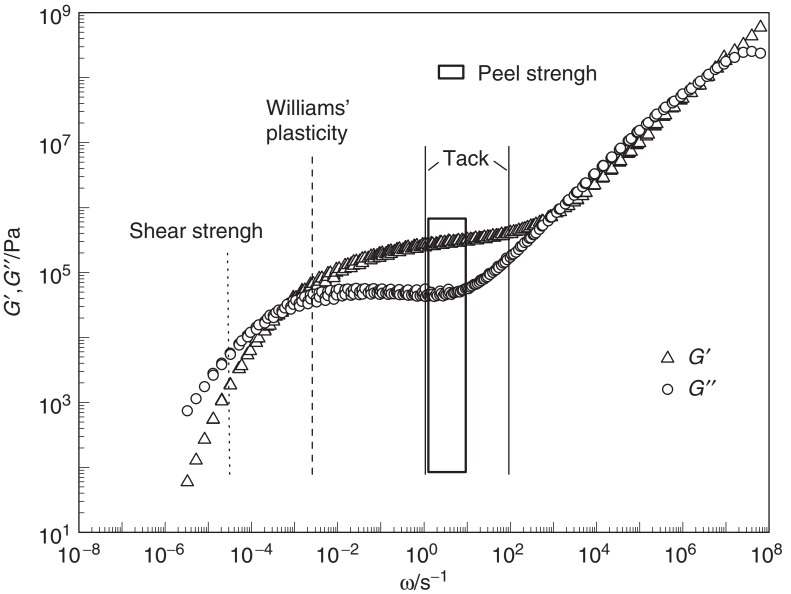


FIGURE 4.1 G', G'' vsersus ω for Oppanol B50. Master curve for T = 25°C. (Modified from Zosel, A., *J. Adhesion*., 44, 6, 1994.)

The viscoelastic properties in the glass transition regime, as well as ω_e and G_0, are independent of molecular weight. In contrast, ω_c^{-1} scales with $M_w^{3.4}$ similar to η_0; as a consequence, the entanglement regime gets broader with increasing molecular weight and the terminal zone is shifted to lower frequencies. This is demonstrated for different grades of Oppanol B in Figure 4.2. Finally, it should be noted that the Cox–Merz rule is valid for PIB and the steady shear viscosity $\eta\ (\dot{\gamma})$ can be calculated from G' and G'' according to [31].

$$\eta(\dot{\gamma}) = |\eta^*|(\omega) = \frac{1}{\omega}\sqrt{G'^2 + G''^2} \quad \text{for} \quad \omega = \dot{\gamma} \tag{4.4}$$

Frequently, the molecular weight of PIB is determined from viscosity measurements of dilute solutions. This method yields the viscosity-average molecular weight, M_v, often provided in data sheets. The zero-shear viscosity of the corresponding melt can be calculated from the intrinsic viscosity [η] determined from dilute solution viscometry. For solutions of PIB in cyclohexane at T_0 = 25°C, the following relation holds [28].

$$\eta_0 = 4.27 \cdot 10^6 \cdot [\eta]^{4.66} \tag{4.5}$$

The adhesive properties of PIB such as tack, shear, or peel resistance are closely related to its viscoelastic and rheological properties outlined above. A rough empirical correlation between relevant shear moduli G' and G'' and different adhesion tests is provided in Figure 4.1. The static shear strength often characterized by a characteristic holding time, t_c, can also be correlated to the steady shear viscosity η at $\dot{\gamma} = 0.1\ \text{s}^{-1}$ [32].

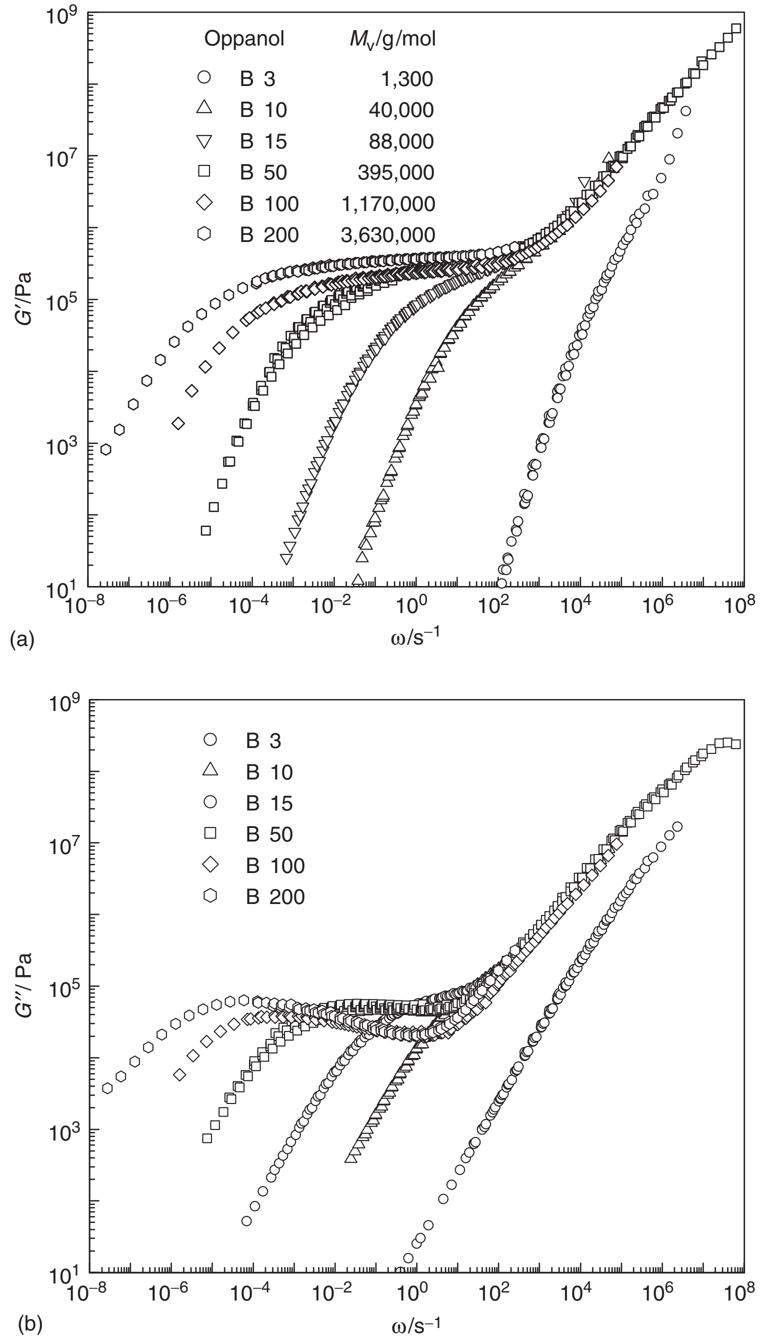


FIGURE 4.2 G' (a) and G'' (b) versus ω for various Oppanol grades.

Zosel [33] calculated the full time dependence of the shear deformation $\Delta l/l_0$, as well as t_c, from $\eta(\dot{\gamma})$ using approximations from linear viscoelasticity and found good agreement with experimental results for materials with low to moderate viscosities, but a significant overestimation of these quantities for high-viscosity PIB ($M_v = 380{,}000$ g/mol).

The resistance to shear increases strongly with molecular weight up to $M_w \approx 10^6$ g/mol and then decreases, accompanied by a transition from cohesive to adhesive failure [32]. Shear resistance can be significantly improved by blending low-molecular-weight species with small amounts of high-molecular-weight grades without a significant change in viscosity.

Peel resistance is another important adhesive property that is closely related to viscoelasticity [34]. Irrespective of test conditions, low-molecular-weight, low-viscosity PIBs exhibit a higher peel resistance than higher-molecular-weight species due to better wetting of the substrate. The transition from cohesive to adhesive failure occurs at room temperature around $M_w = 40{,}000$ g/mol [32]. The deformation of an adhesive across the peel front is mainly extensional [35,36]. Accordingly, Christensen and colleagues [37,38] determined the transient extensional viscosity of PIB mixtures at different strain rates. In combination with appropriate constitutive equations accounting for strain hardening and knowledge of the true shape of the peel front, they were able to establish a model predicting peel force from peel rate, quantitatively.

The peel resistance of PIB on steel can be significantly increased by oxygen plasma treatment of the adhesive, which results in an increase of the carbonyl group concentration in a thin layer (≈100 nm) adjacent to the substrate [39].

Tack is another important criterion for judging adhesive properties of PSAs. Tack is determined by bond formation, as well as bond separation, and hence depends on numerous experimental factors like contact time and force, chemical nature, and roughness of the substrate or debonding rate, but also on PSA properties like viscosity, viscoelasticity, and surface tension. A general review of tack, including a detailed discussion of these aspects, can be found in Ref. [40] (see also *Fundamentals of Pressure Sensitivity*, Chapter 6). Here, we focus on PIB-related tack experiments and their essential results. Tack is characterized by the fracture energy, G_A (often also termed work of adhesion, W_{adh}), which is defined as

$$G_A = \frac{1}{A}\int_0^{t_B} F \cdot \upsilon \, dt = d\int_0^{\varepsilon_B} \sigma \cdot d\varepsilon \tag{4.6}$$

where A is the contact area, F is the force during debonding, υ is debonding rate, t_B is the time of failure, d is the thickness of the adhesive layer, and ε_B is the deformation at failure.

For PIB, as well as for many other polymers, G_A increases with increasing contact time and force. This is especially pronounced on rough substrates for low contact time and force [41]. Furthermore, G_A can be related to the time-dependent stress relaxation modulus $G(t)$, taking into account the true contact area of a rough substrate as a function of contact time and force [42].

In general, bond formation/wetting increases, whereas cohesive and adhesive strength decrease with increasing temperature. Therefore, the fracture energy in a tack experiment is supposed to go through a maximum as a function of temperature. For PIB this

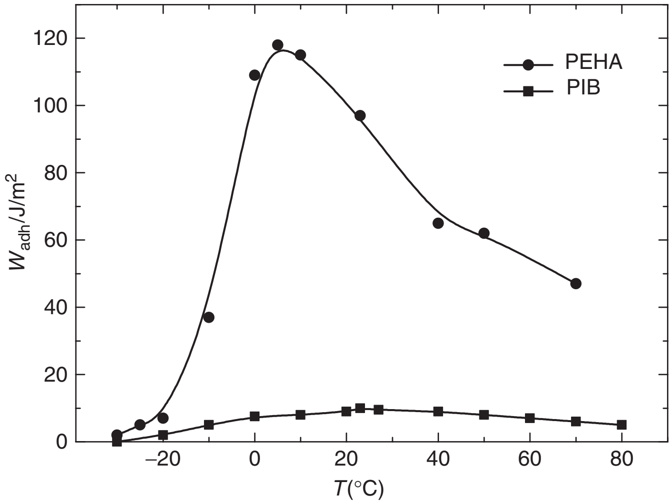


FIGURE 4.3 Adhesive energy, W_{adh}, as a function of temperature for polyethylhexyl acrylate (PEHA) and PIB. (Modified from Zosel, A., *J. Adhesion.*, 30, 143, 1989.)

maximum occurs around room temperature (Figure 4.3) [43]. The fracture energy, G_A, is related to the plateau modulus, G_0, and, according to Dahlquist's criterion [44], a good PSA should have a $G_0 < 3 \times 10^5$ Pa. For PIB $G_0 \approx 3 \times 10^5$ Pa due to its low M_e and, accordingly, pure PIB does not exhibit tack properties typical for PSAs. The debonding process of PSAs in a tack experiment is controlled by cavitation and fibrillation. Cavitation determines the maximum stress occurring during this process, whereas fibrillation results in a subsequent extended stress plateau and usually controls the maximum strain at which failure occurs.

Owing to its dense entanglement network (low M_e), PIB does not form fibrils and the stress versus strain curves during debonding exhibit a sharp maximum but no plateau in the temperature range from −10°C to +60°C, as illustrated in Figure 4.4. This is termed "brittle" failure [45]. Accordingly, the fracture energy is much lower for PIB than for typical acrylate PSAs, as illustrated, for example, in Figure 4.3. Nevertheless, high-molecular-weight PIB grades can serve as a valuable elastomeric basis for PSA formulations, whereas low-molecular-weight grades ($M_v < M_e$) are liquid-like, suitable tackifiers. In the molecular weight range $M_v \geq 50{,}000$ g/mol, the fracture energy [30], as well as the peak stress [32] during debonding, rapidly decay with increasing M_v. This can be attributed [30,32] to the drastic increase in viscosity ($\sim M_w^{3.4}$), which progressively aggravates wetting of the substrate.

PIB can be easily blended with resins, solvents, or other low-molecular-weight components. Thus, the entanglement density can be reduced drastically. As a consequence, the plateau modulus, G_0, decreases (and M_e increases), Dahlquist's criterion is fulfilled, and such mixtures clearly exhibit both cavitation and fibrillation during debonding in tack experiments. This is illustrated in Figure 4.5 for an 80/20 blend of high-molecular-weight PIB ($M_v = 6{,}650{,}000$ g/mol) with another grade with $M_v = 1{,}500$ g/mol (well below M_e).

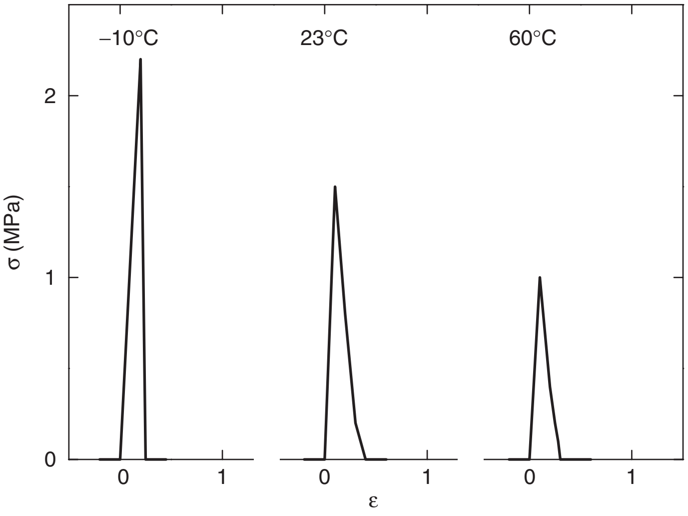


FIGURE 4.4 Probe tack stress–strain curves for PIB during bond separation at various temperatures. (Modified from Zosel, A., *J. Adhesion*, 30, 144, 1989.)

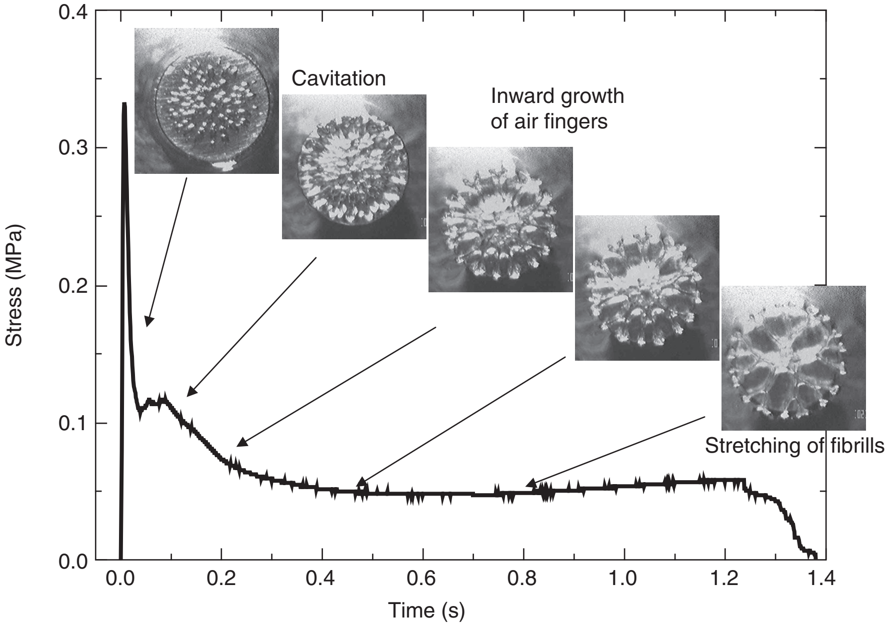


FIGURE 4.5 Cavitation and fibrillation related to characteristic probe tack debonding curve of an 80/20 blend of B1/B6650 at 25°C, F_c = 5N, dwell-time t_d = 1 s, debonding rate v = 1 mm/s. (Modified from O'Connor, A. E., and Willenbacher, N., *Int. J. Adhesion Adhesives*, 24, 338, 2004.)

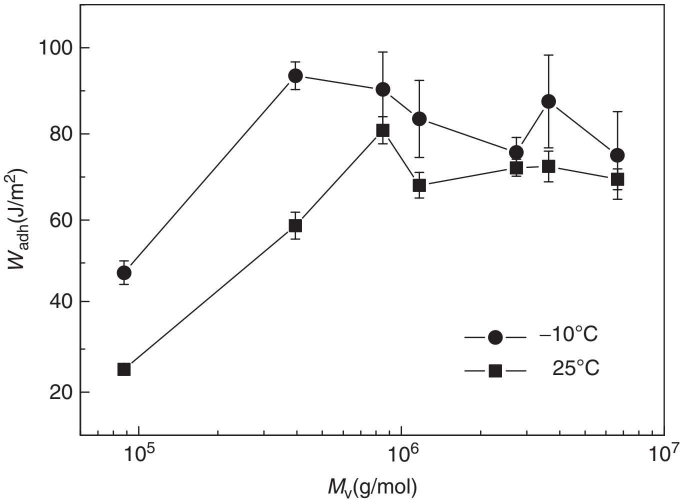


FIGURE 4.6 Adhesive energy, W_{adh}, for the 80/20 blends Bl/BX for samples BX with different M_v at $T = 25°C$ and $-10°C$. Test conditions: $F_c = 2N$, dwell-time $t_d = 1$ s, debonding rate $v = 1$ mm/s. (Adapted from O'Connor, A. E., and Willenbacher, N., *Int. J. Adhesion Adhesives*, 24, 341, 2004.)

Even if Dahlquist's criterion is fulfilled, a minimum molecular weight or number of entanglements per polymer chain is required for fibrillation. As long as the molecular weight is below this threshold, the fracture energy strongly increases but then essentially levels off at higher molecular weight (Figure 4.6).

As previously mentioned, wetting of a substrate by the adhesive is another important parameter controlling tack. In addition to surface roughness and adhesive viscosity, interfacial tension has a strong impact on this phenomenon (see also *Fundamentals of Pressure Sensitivity*, Chapter 1). The surface tension of PIB is 33 mN/m and high tack values are reached if the surface tension of the adherent is close to or higher than this value [43].

The adhesive properties of PIB with a carboxymethylcellulose (CMC) filler have also been investigated [46,47]. Such a composition is widely used as a main component of PSAs suitable for contact with the human body because, apart from the excellent adhesion and physiological neutrality, it is capable of absorbing moisture. Tack and peel resistance have been measured in combination with different substrates and at different bonding/debonding conditions. Cohesive strength is lowered by the presence of the inert CMC component and peel resistance decreases with increasing CMC content, with the exception of high peel rates, where adhesive failure dominates.

A pronounced maximum of the time or strain of failure in tack experiments was determined at a CMC content of about 35%. This again corresponds to the viscoelastic properties of the adhesive, because at this PIB/CMC ratio the plateau modulus, G_0, decreases below Dahlquist's criterion and allows for substantial fibrillation during debonding.

4.4 Conclusions

PIB and the corresponding BRs provide unique properties such as very low moisture and gas permeability, high chemical resistance, and thermal stability; they are odorless, tasteless, and nontoxic and are therefore used in a wide variety of different sealant and adhesive applications. PIB is a linear polymer with a relatively narrow molecular weight distribution. Its amorphous structure and low T_g result in a high permanent flexibility. Various grades covering a broad range of average molecular weight from several thousand to more than 1,000,000 g/mol are commercially available. Systematic research using this broad range of different PIB grades has provided valuable insight into the relationship between viscoelastic and adhesives properties of soft polymers in general and has thus promoted the whole field of research and development of PSAs. More importantly, the availability of these different molecular weight grades offers the advantage of easily tailoring adhesive and cohesive PSA properties, especially in combination with other elastomers, tackifiers, or fillers, to achieve the desired application properties. High-molecular-weight grades serve as a valuable elastomeric basis for PSA formulations; they exhibit a high cohesive strength and demonstrate brittle failure in tack experiments due to the low entanglement molecular weight, M_e. Low-molecular-weight grades are liquid-like, suitable tackifiers and promote wetting and adhesion. PIB is widely used in well-established application areas like building and construction or packaging and tapes. Owing to its nontoxicity, it is approved for food/food contact and thus is of special interest for food packaging. Its stability, damping, and sealing properties make it an interesting material for well-established as well as upcoming automotive applications. Along with the growing market for HMPSAs, PIB will be of increasing relevance. Medical PSA applications will grow, new applications in this area will come up, and, due to its non-skin-irritating and nontoxic features, PIB will be of particular importance in this field.

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