

TAPPI NOTES

1986 Hot Melt Symposium

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1986 Hot Melt Symposium

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ERRATA SHEET
for the "1986 Hot Melt Symposium"

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paraffinic waxes should be used since the latter give brittle formulations. The high capacity for fillers such as calcium carbonate, clay and talc can be used where required. Finally, the excellent compatibility of polybutylene permits modification of various polymers such as APP, block polymers and butyl rubber.

APPLICATIONS

PB 8310 is currently in use for the modification of APP. For economic reasons the amount of polybutylene added to APP is probably restricted to the 5-20% range. Determination of the benefits of polybutylene addition to APP is in progress. Obviously, the addition of polybutylene can be used to adjust the viscosity of the APP. Tensile properties are improved while we also believe that the flexibility and elongation of the APP can be improved by addition of polybutylene. Specific results depend on the type of APP used.

This grade also has potential to upgrade waxes. As shown in Table 10 this work concentrated on tensile properties. Work is in progress to define improvements in wax properties such penetration, congealing point and blocking point using low levels of polybutylene.

PB 8910 (500-1000 dg/min melt index; 10-20 Pa.s neat polymer viscosity) is aimed at the typical hot melt adhesive applications such as product assembly and lamination. It brings a wide service temperature range, high cohesive strength and long open time to these applications. A comparison of some typical properties with an EVA and APP adhesive is shown in Table 11. The polybutylene forms a flexible

adhesive with good SAFT and lap shear strength and yields formulations with low viscosities. It should be noted that a low viscosity can be achieved at

TABLE 10

POLYBUTYLENE BLENDS WITH WAX

FORMULATION

MICROCRYSTALLINE WAX *	70	60	50	40	25
POLYBUTYLENE **	30	40	50	60	75

PROPERTIES

TENSILE YIELD, MPa	0.83	1.17	1.31	1.79	2.21
TENSILE STRENGTH, MPa	<0.03	1.04	1.38	4.76	7.80
ELONGATION @ BREAK, %	2.1		24		180

* SHELLMAX^R 500

** MELT INDEX 15 DG/MIN

TABLE 11

COMPARISON OF ADHESIVE PROPERTIES

PROPERTY	VISCOSITY	SAFT*	LAP SHEAR	COMMENT
UNITS	177°C Pa.s	°C	kN	
POLYBUTYLENE 85°C SP RESIN **	1.2	57	1.47	FLEXIBLE
POLYBUTYLENE 125°C SP RESIN **	2.5	65	--	FLEXIBLE
EVA ¹⁾	1.8	59	2.50	STIFF
APP/POLYBUTYLENE 90/10	5.0	78	0.20	SOFT
* SAFT ON KRAFT/KRAFT				
** FORMULATION POLYBUTYLENE	30			
RESIN	50			
WAX	20			

1) COMMERCIAL EVA ADHESIVE

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HOT MELT THEN AND NOW

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ABSTRACT

This year is being considered the Silver Anniversary of modern day hot melt adhesives. As an adhesive formulator prior to 1960, I have participated in some and witnessed more of the evolving technology of hot melt adhesives. I would share my recollections of the early days and the contrasts observed between our primitive beginnings and today's reality.

Twenty-five years does not seem like a long time to me but my impression is that we have seen great changes over that time interval.

Looking back today, hot melt adhesives were rather primitive when I came on the scene.

I recall hearing of a budding hot melt adhesive manufacturer using a flame fired alkyd kettle to mix a hot melt formulation.

I remember a customer bought an asphalt melting tank from a local roofer to use as a premelter.

I recall a customer developing a dauber applicator by starting with a large steel pan heated on a charcoal fire built in a pit on the plant floor.

A few hazzards but we moved ahead when an early hot melt applicator came on the scene using hot melt broken up by a sledge hammer.

The polymers available to formulate hot melt adhesives were few and narrow in their versatility.

Polyvinyl acetate, ethyl cellulose, polyvinyl butyral, polyethylene, and a few polyamides.

The hot melt applications were similarly few and limited in performance.

Crown cap seals - Heat sealing a polyamide hot melt coated foil disk to the cork liner

Heat seal labels - with a polyvinyl butyral hot melt

Bag lip seals and
Bread end seals - made with an ethyl

cellulose based hot melt

and books that tended to flow apart when made with a polyvinyl acetate hot melt.

Testing too, now looking back, seemed primitive. Your basic Brookfield was available with plenty of spindles. All one had to do is keep the thermometer away from the spindle, while trying to maintain the temperature and read the Brookfield dial.

Then there were diapers--actually they weren't clearly diapers, not diapers at all. But rather the subject of phone discussions about hot melts with an engineer in Cincinnati.

Points like making a polyethylene film bond to non-woven but later peeling it off making it a removable bond added to the interest.

Fortunately, it all worked out very well.

Then came ethylene vinyl acetate, a new polymer. As with most raw materials in those days it was not made intentionally for hot melt adhesives if I recall correctly. I believe it was made as a reinforcing polymer to blend with a nitrocellulose lacquer, later finding its way as a wax reinforcing polymer for such use as frozen food carton coating. Adhesive chemists then started looking at the copolymer--they found that the new copolymer seemed to have marvelous properties. Something entirely different than what we had before. The formulating possibilities opened wide. The variety of products that we were able to make from this copolymer proved that it was indeed a marvelous material.

It seemed this was a key to open several doors--the packaging world, endless opportunities that today still have a broadening future.

The basic characteristics of hot melt adhesives:

Speed of bond formation

Ability to bond impervious surfaces

Gap filling

Water insensitivity

Were translated into essential components of the marketplace.

The engineers, the entrepreneurs, the thinkers, the dreamers, the salesmen, found what hot melts could do to create

modern production lines with the new adhesives, new materials, and new machines.

The need to conserve space and increase productivity, to bond the new surfaces created by the revolution in packaging and converting, all these things provided the impetus, the moving force behind the growth of hot melt adhesives.

The development of truly remarkable hot melt adhesives occurred during the decades following the introduction of ethylene vinyl acetate copolymers.

It was a time of difficulty, a time of challenge with few guidelines, no road maps, little definition, and practically no test procedures.

Because we were traveling down new paths, each new hot melt application had to be studied to define the critical elements required of the adhesive to adequately do the job.

The critical elements had to be translated into laboratory procedures and tests that related to the handling and end use performance.

The tests and procedures that were devised had to be quantified so as to allow reproducible results.

We learned that softening point had little relationship to heat resistance. We had to find the factors that were meaningful. Typically we found that several parameters related to the question and tests had to be devised to measure those parameters.

Good work by competent people like yourselves dealt with those questions.

Early hot melts that were cloudy or separated into 2 or more phases were rejected because of a new criteria of clarity, cleanliness, and stability.

Books now didn't flow apart, nor crack on a chilly day. Magazines were hot melt bound instead of stapled.

New lab equipment with substantial improvements and convenience became available so that today one can practically see the digital readout of the Brookfield thermosol from across the laboratory. Today you don't read the swings of the balance pointer, you observe the digital read out, there is no balance pointer.

As time went on, equipment to make hot melts improved significantly. Hot melts are now automatically cut into convenient pieces, providing easy handling.

A new industry was created in the development and manufacture of hot melt application equipment.

the list of polymers for hot melt adhesives grew and continues to grow including:

Ethylene vinyl acetate acid
terpolymers

Ethylene, ethyl and butyl acrylate
copolymers

Di blocks, tri blocks, multi blocks

High performance polyamides

The endless list just runs off the
slide.

The disposable market blossomed, disposable items being an important part of our way of living, and not just for babies but for an extensive range of needs throughout our life.

New diaper constructions demanded new adhesives.

Applications for hot melt adhesives seemed to be developing at an exponential rate.

The energy crisis and the concern for our environment made solvents scarce, expensive, and undesirable additives to our atmosphere. But these were essential characteristics of the pressure sensitive adhesive business.

Hot melt adhesive, now in the form of a pressure sensitive, as a 100% solids adhesive solved these three problems and provided a production rate previously impractical to obtain.

Base cup attachment added another adhesive to the bottling business.

Hot melt adhesives spread into fields long the domain of water borne adhesives.

Industrial applications broadened the hot melt formulators versatility, air filters, carpet bonding, edge veneering and nail clips are just a few.

Hot melts are used in building houses--stucco reinforcing wire, decorating the outside--shutter assembly, and furnishing the inside--cabinet mirrors.

In the book world, as well as binding the pages in hardbound books, other applications now using hot melt adhesives include tipping, hinging or joints, lining up, case making, and tightbacking.

The conversion of stapling to perfect binding continues.

An expanding market is developing in the automotive field

Corvette seat back bonding carpet to plastic composite

Inner water shields protecting the inside from corrosion

Truck and tail light assemblies

Reactive hot melt, water soluble hot melt, sprayable hot melt

I just do not see an end to the probabilities.

We have reached the silver anniversary and to paraphrase James Graham of Lord Corporation, we are looking to participate in the golden age--the next era.

A time of opportunities, of challenges, or new things and new ways.

POLYBUTYLENE - A NEW POLYMER FOR HOT MELT ADHESIVES

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ABSTRACT

Following preliminary testing of various polybutylene homopolymers and copolymers, a series of ethylene copolymers ranging in melt index from 0.2 to about 5-700 dg/min have been selected for further development for hot melt adhesive applications. These polymers exhibit a very low rate of crystallization in comparison to other polyolefins, which results in hot melt adhesives with long open times. In addition, physical properties fall off only slightly with decreasing molecular weight and flexibility is retained at low viscosity, permitting the development of low viscosity adhesives without loss of performance. The compatibility of polybutylene with a series of tackifying resins is reviewed and applications of polybutylene in the hot melt adhesives field are discussed.

INTRODUCTION

DURAFLEX* polybutylene, a Shell product, has been on the market for several years and is used in applications such as pipe and film. Some time ago we initiated the development of polybutylene for the adhesives market. The unique properties of polybutylene such as slow crystallization rate, good flexibility and retention of properties at high melt index enable the formulation of new adhesive systems with improved performance. The purpose of this paper

*Registered Trademark Shell Oil Company

is to discuss the properties that set polybutylene apart from other polymers used for hot melt adhesives. Although our expertise with polybutylene in hot melt adhesives is limited, the response from our sampling indicates that we are correct in our assumption that polybutylene offers something unique to the hot melt adhesives market.

Polybutylene is a high molecular weight, semi-crystalline polymer derived from 1-butene. It is distinguished from low molecular weight polybutene oils and rubbery higher molecular weight polymers by its higher degree of stereoregularity. The stereoregularity allows crystallization to occur which is, at least partly, responsible for the unique properties of polybutylene. The degree of stereoregularity of polybutylene can be controlled by modification of the catalyst or via copolymerization with various monomers. This permits development of a variety of polymers having a wide range of properties. The physical properties of polybutylene homopolymers and ethylene copolymers are given in Table 1.

EFFECT OF POLYBUTYLENE PROPERTIES ON ADHESIVES

The polybutylene properties that are important from an adhesives point of view are summarized in Table 2. Slow crystallization results in long open times and allows adhesion to cold substrates. The polymer is compatible with aliphatic tackifying resins rather than with the more polar resins. In addition, polybutylene shows good compatibility or can be blended well with other polymers. Polybutylene also accepts very high filler loading levels. Blends with as much as 80%w fillers have been prepared. These blends retain flexibility and possess good properties.

TABLE 1

TYPICAL PHYSICAL PROPERTIES OF POLYBUTYLENE RESINS

PROPERTY UNITS	MELT INDEX DG/MIN	T _m °C	T _g °C	TENSILE PROPERTIES			
				CRYST. %	YIELD MPa	BREAK MPa	ELONG. %
POLYBUTYLENE HOMOPOLYMER	2-20	125	-25	55	13.8	29-31	350
BUTENE/ETHYLENE COPOLYMER	0.2-700	99-102	-34	35	4-4.5	10-24	3-600

The aliphatic hydrocarbon structure of polybutylene results in a non-corrosive polymer. This is important in applications where the polymer is in contact with metal substrates (automotive, construction and appliance sealants). The same structure also provides good thermostability of the polymer, good adhesion to non-polar substrates and a low MVTR. The combination of a high degree of isotacticity with ethylene incorporation into the polymer yields a glass transition temperature of -35°C and a melting point of about 100°C which, together with retention of properties close to the melting point, results in a wide service temperature range. Finally, the conventional application techniques can be used with polybutylene. The products are sprayable and form excellent foams.

CRYSTALLIZATION BEHAVIOR OF POLYBUTYLENES

One of the unique features of DURAFLEX polybutylene is its crystallization behavior. In comparison to polyethylene, polypropylene and EVA, polybutylene crystallizes very slowly. At a temperature of 90°C the homopolymer has a crystallization half

time of about 10 minutes. The ethylene copolymers crystallize slower and have a half time of more than 30 minutes. The crystallization rate increases with lower temperatures and reaches a maximum at room temperature, but even then the crystallization is slow (Figure 1).

For applications where a more rapid crystallization is required, e.g., in product assembly, the rate of crystallization can be increased by nucleation. The addition of low molecular weight polyethylene or stearamide reduces the crystallization half time at room temperature from 10 to 2 minutes. The presence of compatible tackifying resins, however, lower the rate of crystallization, while non-compatible resins have less effect on crystallization rate. In other words the crystallization behavior of polybutylene can be tailored to a particular application through proper formulation.

Polybutylene crystallizes from the melt in the so called crystalline form II and slowly transforms into form I. Form II is lower melting and has lower tensile strength and modulus than form I. The transformation half time of the

TABLE 2

SUMMARY OF POLYBUTYLENE PROPERTIES

<u>POLYMER</u>	<u>ADHESIVE</u>
SLOW CRYSTALLIZATION	LONG OPEN TIME STRESS RELIEF IN BOND LINE (NON-BRITTLE AT INTERFACE) ADHESION TO COLD SUBSTRATES
COMPATIBILITY	COMPATIBLE WITH ALIPHATIC RESINS LIMITED COMPATIBILITY WITH POLAR RESINS COMPATIBLE WITH APP, WAXES, PIB, BUTYL RUBBER, EPDM, BLOCK POLYMERS HIGH FILLER LOADINGS POSSIBLE
NON-POLAR STRUCTURE	ADHESION TO NON-POLAR SUBSTRATES GOOD THERMAL STABILITY NON-CORROSIVE
WIDE MELT INDEX RANGE FROM 0.2-1000 DG/MIN	FLEXIBLE AT LOW VISCOSITIES WIDE LATITUDE IN FORMULATION TO BALANCE COHESIVE/ADHESIVE STRENGTH AND VISCOSITY LOW MVTR
LOW T_g , HIGH T_m	WIDE SERVICE TEMPERATURE RANGE

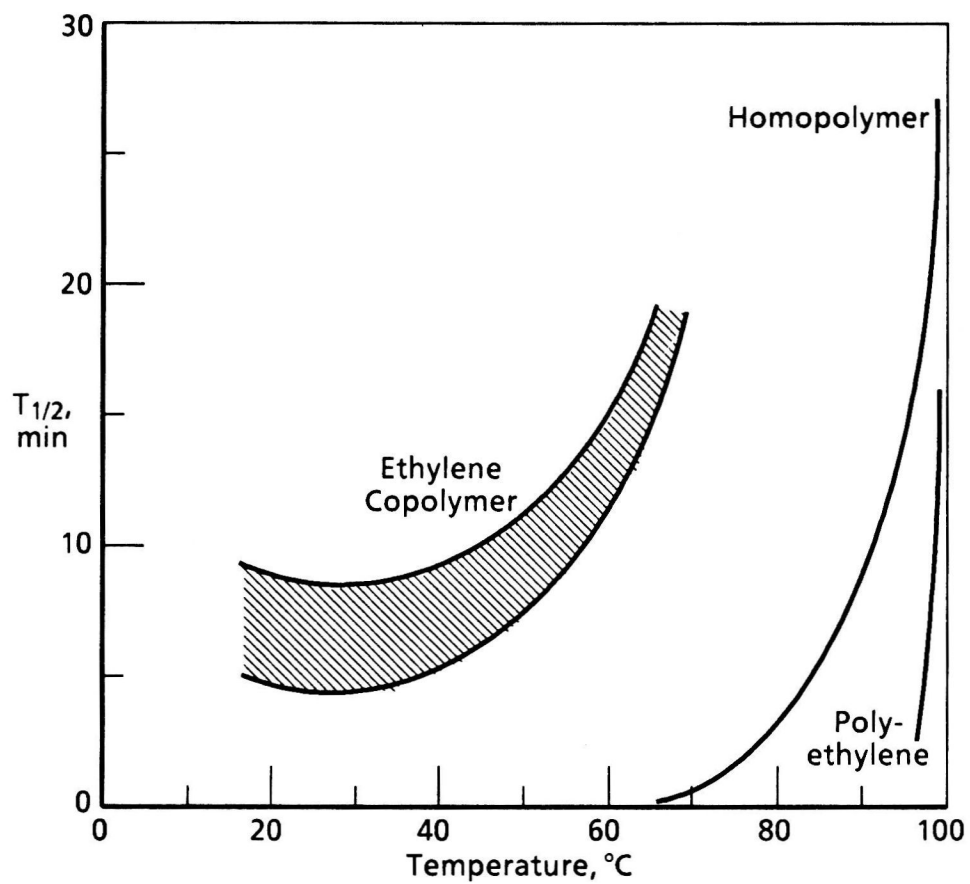


Figure 1. Crystallization Half Times of Polybutylene from Melt

09252-1

transition from form II to I is in the order of half a day at room temperature. As a result strength and modulus increase with time, a phenomenon which should be taken into account when testing polybutylene based formulations.

The slow crystallization of polybutylene can be used to formulate adhesives with long open times. This behavior is most apparent in contact adhesive type of applications. Table 3 shows the effect of the ethylene copolymer on the open time of the polymer.

The slow crystallization also permits bonding to cold, heat sink type substrates (see Table 3). The bond forms slowly and the low crystallization rate provides stress relief, which avoids the development of brittleness. This behavior is also demonstrated by the increase in hardness with time

Figure 2 shows the Shore A hardness for a copolymer quenched from 200°C to room temperature. During the first few minutes the product is very soft. After 3-5 minutes a reasonable degree of hardness is developed that slowly continues to increase.

DEVELOPMENT OF A GRADE LINE

Initially, homopolymers and other ethylene copolymers were considered for hot melt adhesive applications. The lower rate of crystallization of the polymers with higher ethylene contents permit the formation of flexible adhesive products and we have concentrated our efforts therefore on these copolymers.

In addition, it was recognized that low viscosity products were essential to penetrate the hot melt adhesives market. A series of products was prepared with melt indices ranging from 1 to 1000 dg/min and sampled to a variety of customers. The Brookfield viscosity of these products as a function of melt index is shown in Figure 3. This figure demonstrates the large range in viscosities that are available.

The relationship between melt index and melt viscosity shows a sharp discontinuity at a melt index of about 100 dg/min. Below a melt index of 100 dg/min the product can be expected to be more elastic due to the presence of higher molecular weight chains.

The properties of the various grades are shown in Table 4.

TABLE 3

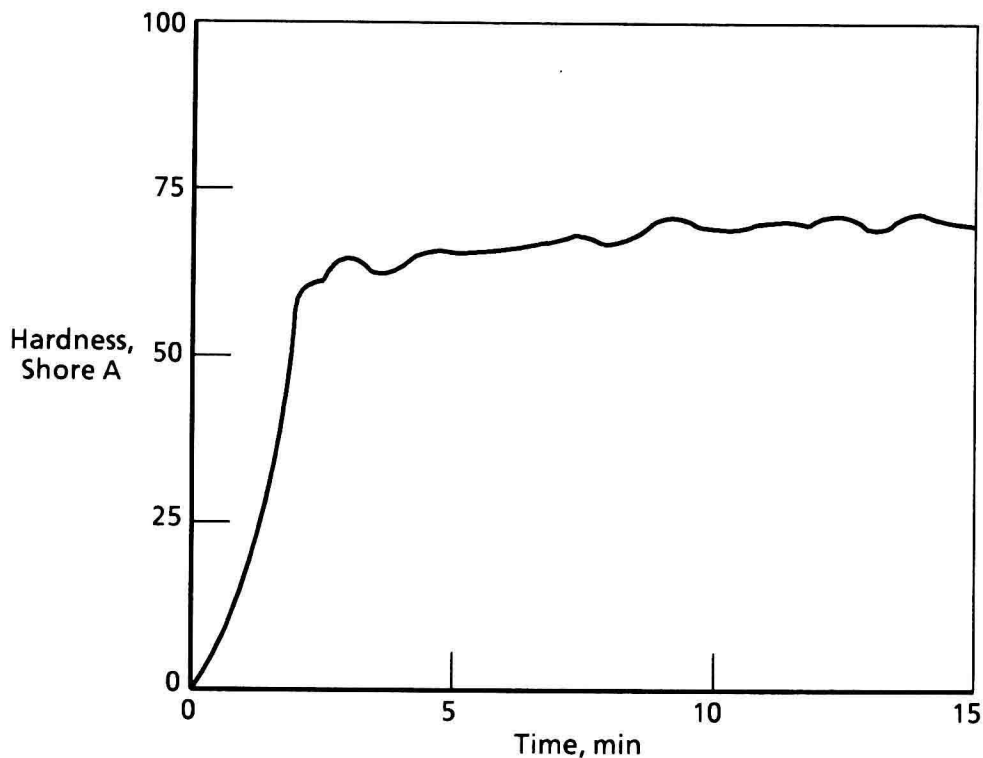
OPEN TIME AND ADHESION TO COLD SUBSTRATES AS A FUNCTION
OF ETHYLENE CONTENT OF POLYBUTYLENE RESINS

PROPERTIES UNITS	OPEN TIME MINUTES	ADHESION TO COLD**	
		ALUMINUM	STEEL
PE ADHESIVE	<1	NO	NO
EVA ADHESIVE	<1	YES	NO
POLYBUTYLENE HOMOPOLYMER	30-40	NO	NO
BUTENE/ETHYLENE COPOLYMER	>300	YES	YES

* FORMULATION:

POLYBUTYLENE 50 %
ARKON P85 50 %
ANTIOXIDANT 0.3 PHR

** ADHESION MEASURED BY HAND TEST



**Figure 2. Polybutylene Crystallization
Hardness vs. Time**

TENSILE PROPERTIES OF THE POLYBUTYLENE COPOLYMERS

Polybutylenes retain a substantial portion of their physical properties at low molecular weights. Tensile yield values remain at essentially the same level of 4.0-4.5 MPa over the entire melt index range. Tensile strength and tensile elongation drop only slightly over this range. (see Figure 4-6). Many polymers show a much faster drop in properties when the molecular weight is lowered. Furthermore, the polybutylene copolymer remains a soft, pliable polymer even at low molecular weights and develops no sign of brittleness.

BLENDED OF POLYBUTYLENE GRADES

We have determined that products with intermediate viscosities can be manufactured via blending. An extreme case was selected to demonstrate this capability. An 18 melt index product was blended with a 930 melt index product to various melt index levels. Properties of the blend were compared with those measured on polymers produced directly to the desired melt index. As is shown in Figure 4-7, very

TABLE 4

TYPICAL PROPERTIES OF POLYBUTYLENE GRADES

		MELTING POINT, °C		95-98	
		GLASS TRANSITION POINT, °C		-35	
		CRYSTALLINITY, %		35	
UNITS	MELT INDEX	TENSILE PROPERTIES			MELT VISCOSITY
GRADE	DG/MIN	YIELD	BREAK	ELONG.	@ 177°C
		MPa	MPa	%	Pa.s
PB 8010	0.25	4.5	24.1	590	-
PB 8310	3.2	4.5	24.1	550	-
PB 8410	20	4.3	22.1	500	1000
PB 8510	45	4.1	19.3	400	600
PB 8910	700	4.0	10.4	350	10-20

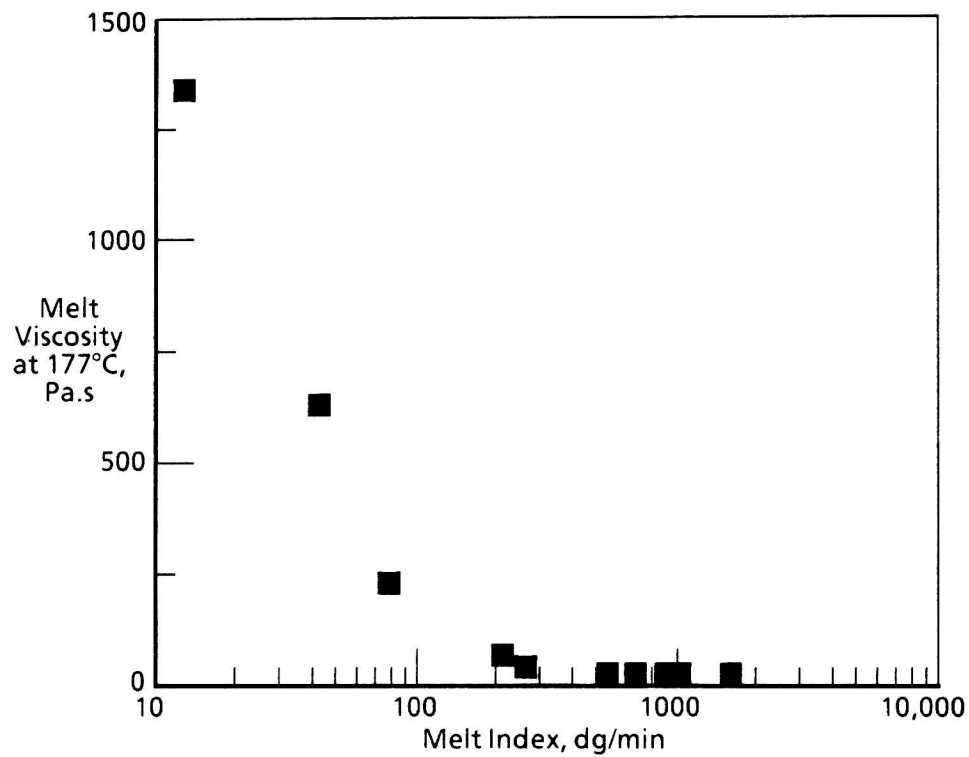


Figure 3. Polybutylene Melt Viscosity
Viscosity at 177°C vs. Melt Index

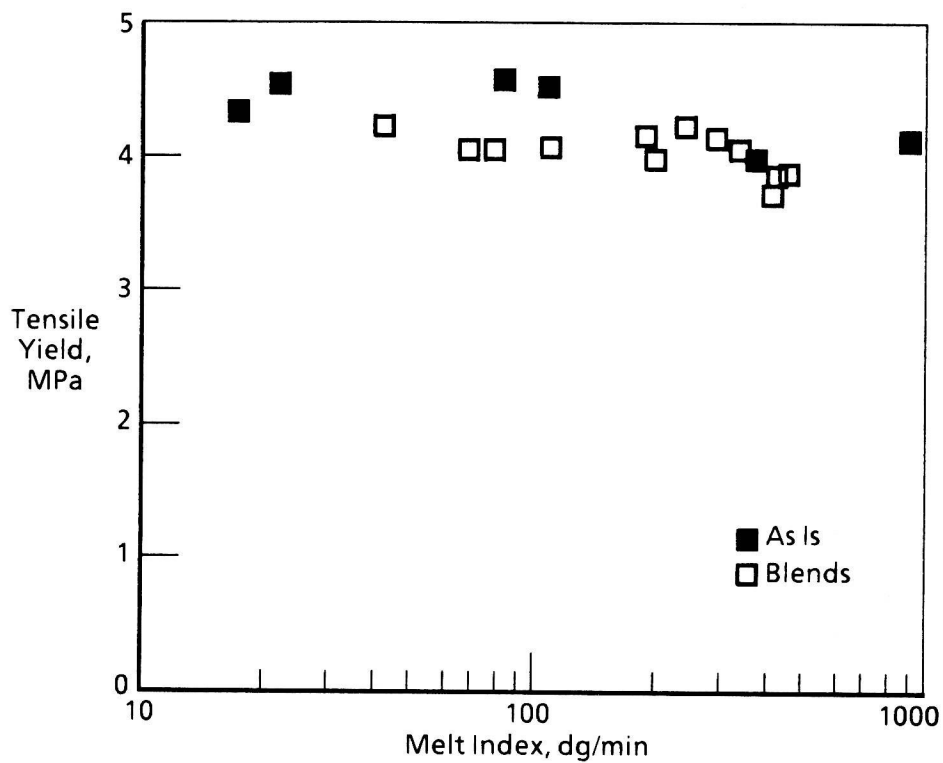


Figure 4. Polybutylene Tensile Yield

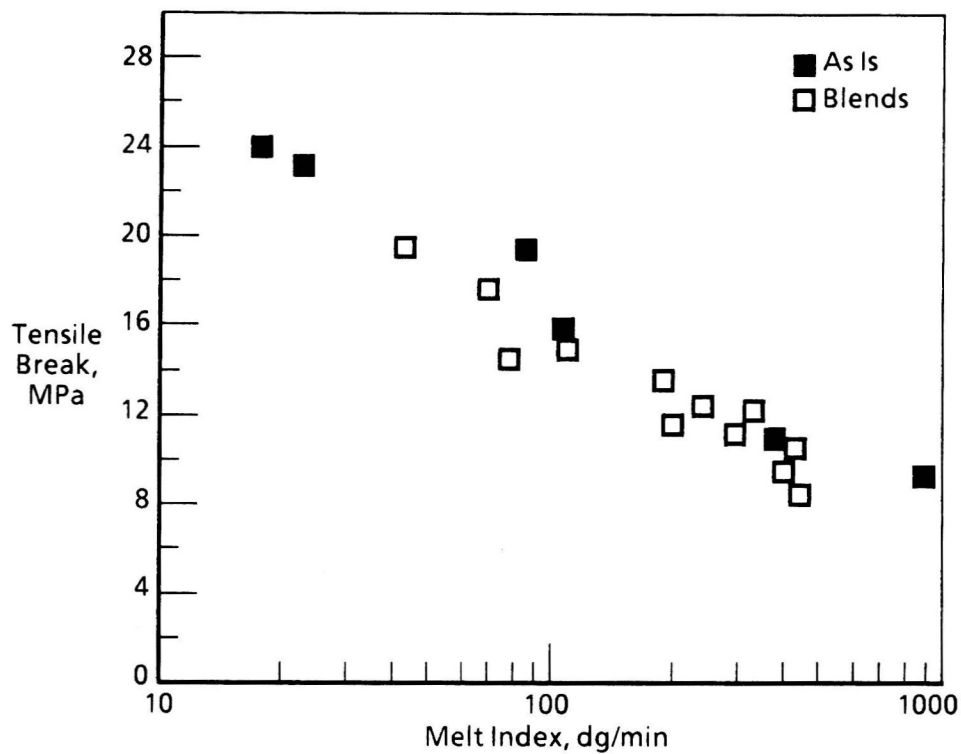


Figure 5. Polybutylene Tensile Break

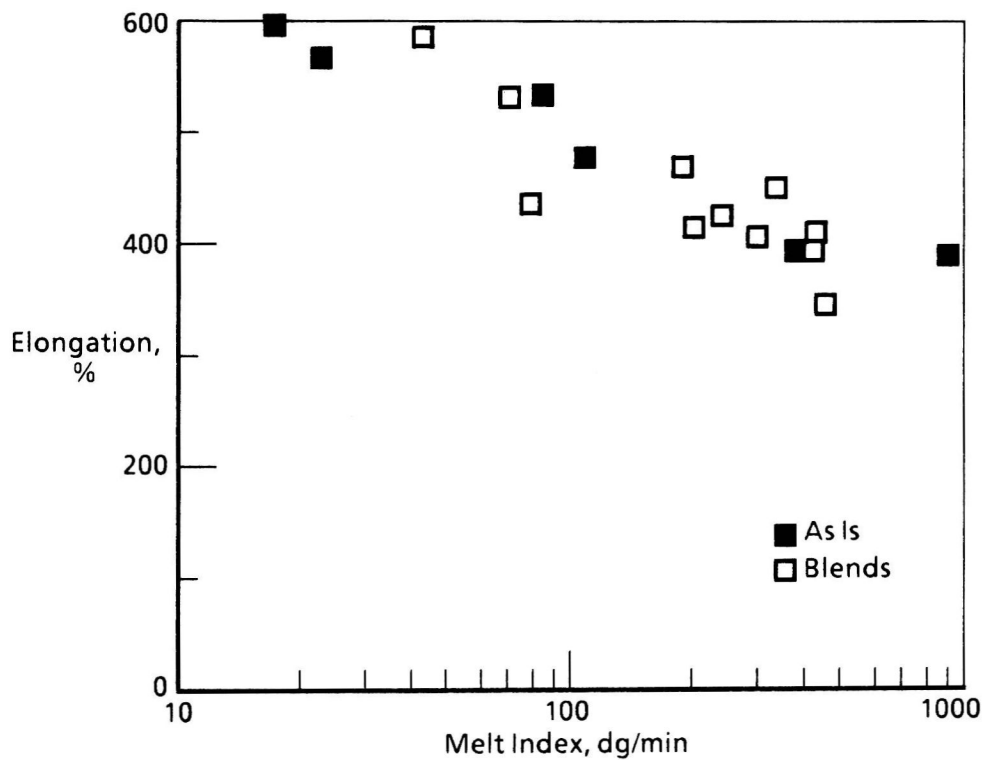


Figure 6. Polybutylene Tensile Elongation

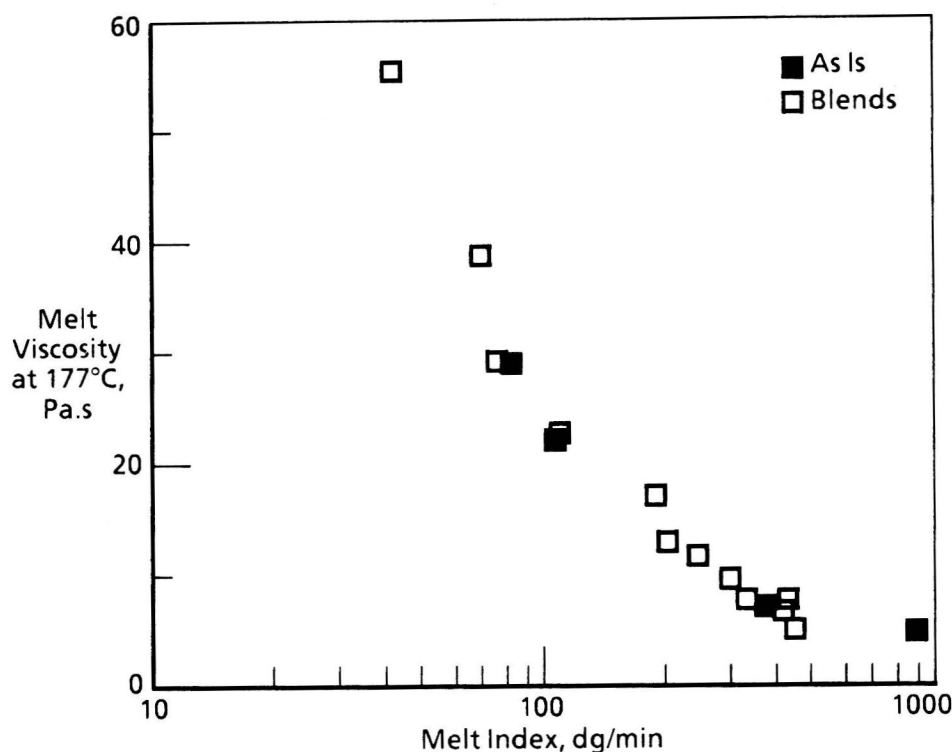


Figure 7. Viscosity Polybutylene/Arkon P85 50/50 Blends

little difference in both melt viscosity of blends with tackifying resins and tensile properties can be observed. Due to the presence of higher molecular weight material, however, the blends show a somewhat more elastic behavior. We do not expect this difference to be noticeable in most applications. By using this technology therefore, the inventory at the formulator can be limited to two or three products with the opportunity to formulate a wide variety of viscosities.

RESIN COMPATIBILITY

Compatibility with tackifying resins plays an essential role in the development of a hot melt adhesive. Polybutylene with its aliphatic structure is compatible with a variety of aliphatic resins, C5-C9 resins, hydrogenated resins and in some cases with polyterpenes. For our study, 25/75, 50/50 and 75/25 blends of polybutylene with tackifying resins were made. Two grades of polybutylene were selected for the study, a product with a 20 and one with a 1000 melt index. Since most formulators are familiar with EVA in hot melts, we have included a high flow, 28% vinylacetate EVA for comparison. The tackifying resins selected for our compatibility study are listed in Table 5. The first part of the study consisted of

TABLE 5
COMPATIBILITY STUDY
TACKIFYING RESINS USED IN STUDY

RESIN	TYPE	MELTING POINT, °C
WINGTACK PLUS	ALIPHATIC RESIN	94
ESCOREZ 1304	ALIPHATIC RESIN	100
ARKON P85	HYDROGENATED AROMATIC	85
REGALREZ 1078	HYDROGENATED AROMATIC	78
FORAL 105	HYDROGENATED ROSIN ESTER	105
PICCOLYTE S115	POLYTERPENE	115
HERCOTAC AD1100	MODIFIED AROMATIC	96
ZONESTER 85	ROSIN ESTER	85
PICCOFYN D125	TERPENE PHENOLIC	125
KRISTALEX 3070	STYRENIC	75