

Polyolefin Waxes*

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Synopsis

The properties of polyolefin waxes derived from polypropylene, polybutene, and their copolymers are described, with particular reference to those which are useful as coatings and barrier materials. These products can be applied with conventional melt- and curtain-coating machines on paper and other substrates to give coatings with properties comparable to those of extrusion-coated, plastic-grade polyolefins. Because of their low melt viscosity and consequent ease of application, they should find wide application in the packaging industry.

INTRODUCTION

The development of new catalysts and processes for the polymerization of olefins to solid, crystalline polymers has made possible a concurrent development in the synthetic wax field. The preparation and properties of crystalline waxes from polypropylene has been described in a previous publication.¹

This material is now available in commercial quantities from Eastman Chemical Products, Inc. Polypropylene wax shows promise for application in a wide variety of industrial applications because of its high melting and blocking temperatures, low melt viscosity, and good electrical and barrier properties. It is useful in hot-melt coatings for paper, paper board, foil, and other substrates because of its nontoxicity and the toughness of the coating derived when the melt is chilled rapidly. The coating so formed is comparable in physical properties with those obtained from extrusion coatings of plastic-grade polyolefins.

However, polypropylene wax has limitations. In some applications its melting point is too high for use in existing hot-melt machines, and its molecular weight must be such that its melt viscosity is above 3000 cp. at 190°C. if a tough coating is to be obtained. Furthermore, the coating tends to embrittle if stored for extended periods of time at elevated temperatures. It is also desirable in some applications, for example, in curtain

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TABLE I
Properties of Olefin Waxes

Composition, % butene	Inherent viscosity	Annealed density, g./ml.	Melt viscosity at 190°C., cp.	Melting point, °C.	Penetration		Tensile modulus, psi ^a	Tensile yield strength, psi ^a	Elongation, % ^a
					hardness, mm. × 10 ⁻¹ 250 g./ 5 sec./ 25°C.	5 sec./ 25°C.			
0	0.42	0.914	7,500	158-161	0.0	0.0	91,000	2,070	425
5	0.46	0.909	11,000	146-151	0.0	0.0	35,000	1,260	635
20	0.43	0.890	10,000	128-145	1.5	1.5	20,000	834	655
50	0.34	0.886	3,200	94-118	14.0	14.0	7,800	242	435
100	0.4	0.906	8,000	104-108	2.5	2.5	40,000	2,100	40

^a Measured on quenched 1-mil films.

coating, to have a coating which does not require a quench roll to give a tough film.

These deficiencies were overcome by using low-viscosity copolymers of 1-butene (hereafter referred to as butene) and propylene. These products were found to show better toughness at low melt viscosities and, if enough butene is included, do not require as much quenching to give tough coatings. These improvements are obtained with some reduction in the tensile strength, hardness, and stiffness of the coating. Because of their lower melting points these waxes can be coated at lower melt temperatures than polypropylene wax.

Typical properties of low-viscosity propylene-butene copolymer waxes are shown in Table I along with those of polypropylene and polybutene waxes. The table shows that the melting point of the polymer decreases with increasing amounts of butene in the copolymer until, at 50% butene, the melting point is lower than that of either homopolymer. The penetration hardness, tensile strength, and modulus of quenched films show a similar relationship. The increase in toughness is not evident from this table. However, this shows up clearly if the properties of air-quenched films, shown in Table II, are compared.

A further advantage is that the molecular weight of the copolymer waxes can be reduced to a lower level while still retaining good toughness in the quenched coating. This is shown in Table III where the elongation of a

TABLE II
Properties of Air-Quenched Films of Polyolefin Waxes

Com- posi- tion, % butene	Melt viscosity, cp.	Modulus, psi	Tensile strength, psi	Elon- gation, %
0	7,500	Too brittle to test	Too brittle to test	0
5	11,000	Too brittle to test	Too brittle to test	0
20	10,000	82,000	1,600	4
40	2,900	31,000	1,120	110
100	10,000	33,000	1,650	10

TABLE III
Elongation of Quenched Films

Composition, % butene	Melt viscosity at 190°C., cp.	Elongation, %
0	7,500	425
0	3,000	289
0	1,000	0
20	10,000	655
20	3,200	540
20	1,300	36

quenched film is used to indicate toughness. Whereas coatings from low-viscosity polypropylene become brittle if the melt viscosity of the polymer is less than about 3000 cp., 20% butene copolymer will give tough coatings at melt viscosities as low as 1300 cp. This lower viscosity allows the coating of thinner films at faster rates with obvious commercial advantage.

POLYBUTENE WAXES

Low-viscosity crystalline polymers of butene have not been described previously. They have a number of unique properties. Physical properties of the bulk polymer and of quenched films are shown in Table IV. Although the elongation of the quenched film from the 2200-cp. material is low, it has been found that this material, when coated on paper, will pass conventional crease tests. Furthermore, the coated paper retains this ability after prolonged storage at room or elevated temperatures. This is surprising in view of the marked changes in crystalline form which take place in the polymer after coating. The quenched film, for example, undergoes a slow crystallization at room temperature which results in a considerable change in properties. This is shown by the data in Table V. Here the elongation drops from 200 to 10% after storage at room temperature for five days. At the same time, the modulus and tensile strength increase by a factor of about two.

This is a further manifestation of the crystalline phase changes which take place when molten polybutene is cooled. The polymer first crystallizes in the structure which has been designated "form 2," which is unstable and slowly converts to "form 1."² This is shown in the x-ray diffraction patterns of quenched, air-quenched, and aged films given in Figure 1. The quenched film shows relatively broad peaks (caused by small or imperfectly formed crystallites) of both form 2 and form 1. The

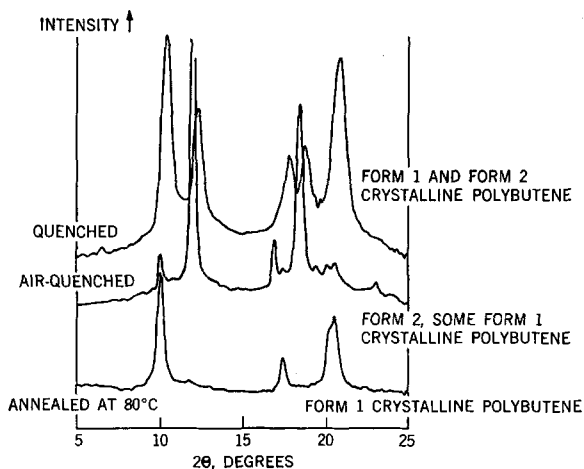


Fig. 1. X-ray diffraction patterns of polybutene wax films.

TABLE IV
Properties of Polybutene Waxes

Inherent viscosity	Annealed density, g./ml.	Melt viscosity at 190°C., cp.	Melting point, °C.	Cloud point, °F. ^a	Modulus, psi	Tensile yield, psi	Elongation, %
0.39	0.906	8,000	104-108	453	40,000	2,100	40
0.40	0.907	5,000	107-111	149	41,200	1,970	26
0.34	0.903	2,200	110-114	156	45,400	1,520	5

^a In 130°F. paraffin wax at 2% concentration.

TABLE V
Crystalline Phase Change in Polybutene Waxes (Melt Viscosity,
3,400 cp. at 190°C.)

Time, after casting	Modulus, psi	Tensile yield, psi	Elongation, %
1 hr.	25,000	910	200
5 days	45,000	1,600	10

air-quenched film, if inspected immediately, shows mostly the form 2 polybutene. Annealing for approximately 150 hr. at 80°C. converts all of the form 2 to the form 1 type. When it is in the form 2 state, the coating is quite "sticky" and it retains this condition for 10-60 sec. even after cooling to room temperature. This "delayed action" is an advantage in a melt adhesive but causes trouble if paper coatings are made at high linear rates since the roll will tend to block.

A further unique characteristic of polybutene wax is its excellent compatibility with paraffin wax and other synthetic and natural wax products. This is demonstrated by the "cloud point" in paraffin wax, listed in Table VI, which is only slightly above the melting point of the paraffin used in the test. This makes polybutene wax of considerable interest as a blending agent in paraffin and other wax coatings.

TABLE VI
Cloud Point of Polybutene Wax Blends With Paraffin Wax
Polybutene Inherent Viscosity, 0.36;
Melt Viscosity, 10,000 cp. at 190°C.

Concentration of polybutene wax, %	Cloud point, °F.
0	133
2	140
5	140
10	140
20	143
40	149

AGING CHARACTERISTICS OF LOW-VISCOSITY POLYOLEFINS

As explained previously, one of the undesirable characteristics of low-viscosity polypropylene films is that they tend to embrittle when aged at elevated temperatures. Films made from copolymer waxes are much more stable towards embrittlement. This is shown in Table VII. It can be seen that, while polypropylene and the 5 and 20% butene copolymers became brittle at 0.7, 1.8, and 3.1 hr. at 80°C., the 40% copolymer and the polybutene failed only after 120 hr. In these latter two cases it is possible that the failure was due to oxidative degradation rather than crystallization, although this point has not yet been established unequivocally.

TABLE VII
Embrittlement of Low-Viscosity Polyolefin Films at 80°C.

Wax composition, % butene	Melt viscosity, cp. at 190°C.	Embrittlement time, hr.	Density at failure, g./ml.
0	3,000	0.7	0.895
5	1,500	1.8	0.894
20	2,600	3.1	0.893
40	2,900	>120	0.892
100	3,750	>120	0.907

The rate of crystallization for a 40% butene copolymer at various temperatures is shown in Figure 2. It shows a similar rate behavior to that described previously for polypropylene wax.¹

X-ray diffraction patterns of the films confirm that the embrittlement is caused by changes in the crystalline structure of the material. These

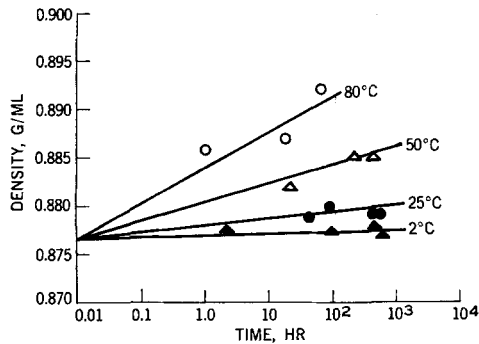


Fig. 2. Crystallization of 40% butene-propylene copolymer wax.

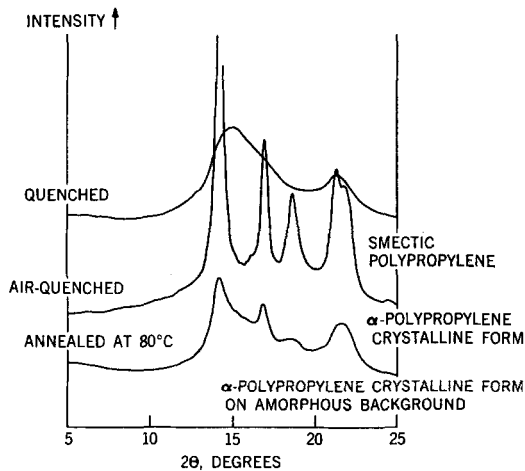


Fig. 3. X-ray diffraction patterns of polypropylene wax films.

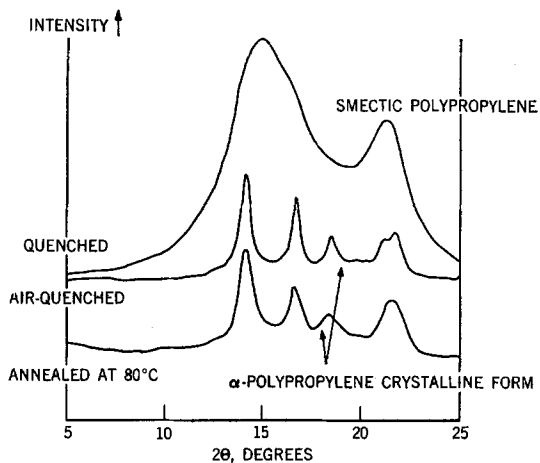


Fig. 4. X-ray diffraction patterns of 20% butene-propylene copolymer films.

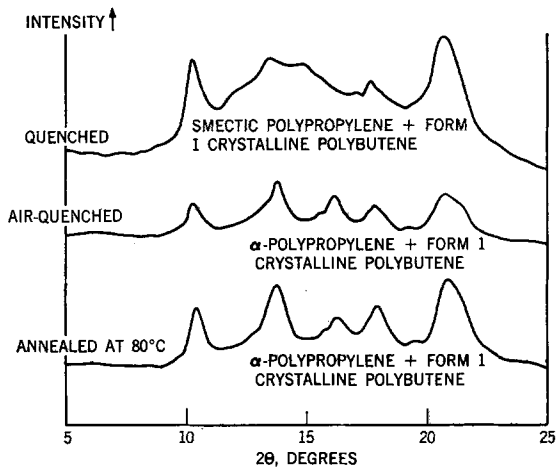


Fig. 5. X-ray diffraction patterns of 40% butene-propylene copolymer films.

are shown for polypropylene film, 20% butene-propylene copolymer film, and 40% butene-propylene copolymer film in Figures 3, 4, and 5. In quenched polypropylene only the amorphous peaks characteristic of the so-called smectic state are observed. Air-quenching gives rise to strong, sharp rings characteristic of the α -polypropylene crystalline form. If the quenched film is annealed at 80°C. for an hour or more, strong α -polypropylene peaks develop. The quenched 20% butene copolymer shows only the smectic polypropylene form. An air-quenched sample shows the development of the α -polypropylene crystallinity, although the peaks are not as intense as in polypropylene. Annealing the quenched film gives a similar degree of crystallinity. The 40% copolymer shows the presence of both smectic polypropylene and form 1 polybutene in the quenched film.

Air-quenching from the melt or annealing for 140 hr. at 80°C. gives a film showing peaks corresponding to both α -polypropylene and form 1 polybutene crystallinity.

PERMEABILITY

One of the important characteristics of a plastic film used in packaging is its permeability to various gases or liquids. The water vapor and oxygen transmission of a number of plastic films and quenched films of polypropylene, polybutene, and copolymer waxes are compared in Table VIII. It can be seen that the permeability of copolymers containing up to 20% butene is very nearly the same as that of either plastic-grade or low molecular weight polypropylene. Even with 40% butene in the copolymer, the permeability is increased only by a factor of about two, which is still adequate for many uses.

TABLE VIII
Permeability of Polyolefin Films

Material	Moisture permeability ^a	Oxygen permeability ^b
Low-density polyethylene plastic	0.44	7.8
Medium-density polyethylene plastic	0.20	4.1
Polypropylene plastic	0.32	5.1
Polypropylene wax (quenched)	0.31	5.0
5% Butene copolymer wax (quenched)	0.40	5.2
20% Butene copolymer wax (quenched)	0.43	5.5
40% Butene copolymer wax (quenched)	0.63	11.1
Polybutene wax (quenched)	0.49	7.4

^a Values given in [g.-cm./cm.²-hr.-mm. (Hg)] $\times 10^6$ (at 90% relative humidity, at 100° F.).

^b Values given in [cc.-mil/m.²-atm.-day] $\times 10^{-3}$.

CURTAIN COATING

Materials previously described have been generally of the type which requires quenching in order to give tough, heat-sealable films. Such coatings can be readily applied by conventional melt-coating techniques involving an applicator roll or a slit die followed by a quench roll. However, in some cases it is not convenient or practical to quench the coating with a chill roll after application to the substrate. This is the case, for example, in curtain coating in which the package is conveyed through a moving, thin film or "curtain" of molten polymer. A sketch of a typical curtain-coating machine is shown in Figure 6. In this machine the quenching is obtained by means of the heat removed by the coated article or by additional air or water cooling.

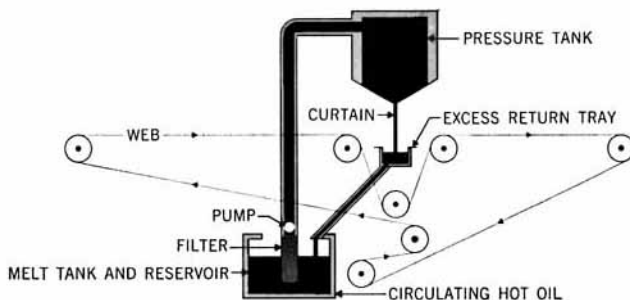


Fig. 6. Pressure curtain coater.

Propylene copolymer waxes containing 30–50% butene are ideal for use in such machines since they have low melt viscosities, yet they give tough films without extensive quenching (see Table II). In view of their potential low cost and outstanding physical properties, these resins are expected to be widely used in such applications in the near future.

CONCLUSION

The properties of polybutene wax and butene–propylene copolymer waxes have been described with particular reference to those which suit them for use as coatings and barrier materials. These products can be applied on paper and other substrates with conventional melt and curtain-coating machines, to give coatings with properties comparable to those of extrusion-coated, plastic-grade polyolefins. Because of their low melt viscosity and consequent ease of application, they should find wide application in the packaging industry.

EXPERIMENTAL

Polymer Preparation

The olefin copolymer waxes were made by copolymerization of propylene and butene using an organometallic catalyst system, followed by thermal degradation (if necessary) to the desired molecular weight by a procedure described in our previous publication.¹

Film Preparation

One- to two-mil wax films were coated on a hot, ferrotype plate using a heated doctor blade. The plate was then quenched in an ice-water bath and the film stripped off for testing. Physical properties were determined on 1/2-in. strips in an Instron testing machine. Permeability measurements were made by ASTM standard methods.^{3,4} The x-ray diffraction measurements were made on 1-mil films using a General Electric Model X-RD-5 x-ray diffraction unit with a Geiger detector.

References

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2. R. Zannetti, et al., *Chim. Ind. (Milan)*, **43**, 735 (1961).
3. ASTM Standard Method E-96-53T.
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Résumé

Les propriétés de cires de polyoléfines dérivées du polypropylène, polybutène et de leurs copolymères sont décrites avec une référence particulière pour celles qui sont utiles aux matériaux de recouvrement et de protection. Ces produits peuvent être appliqués avec des machines conventionnelles de fusion et de revêtement pour papier et d'autres substrats en vue de produire des revêtements possédant des propriétés comparables à celles obtenues par extrusion des polyoléfines plastiques. A cause de leur faible viscosité à l'état fondu et par conséquent de leur facilité d'emploi, ces produits pourraient trouver une large application dans l'industrie de l'emballage.

Zusammenfassung

Die Eigenschaften von Polyolefinwachsen, welche sich von Polypropylen, Polybuten und ihren Copolymeren ableiten, werden mit besonderer Berücksichtigung der als Beschichtungs- und Abgrenzungstoffe brauchbaren beschrieben. Diese Produkte können mit konventionellen Schmelz- und Kurtinenbeschichtungsmaschinen auf Papier und andere Substrate aufgetragen werden und liefern Überzüge, deren Eigenschaften mit denjenigen extrusions-aufgetragener plastomerer Polyolefine vergleichbar sind. Wegen ihrer niedrigen Schmelzviskosität und dadurch bedingten leichten Anwendbarkeit sollten sie in der Verpackungsindustrie eine weite Anwendung finden.

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