

Modification of a Fischer-Tropsch Wax by Grafting with Maleic Anhydride

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ABSTRACT: The polarity of a hard Fischer-Tropsch paraffin wax was improved through grafting of maleic anhydride (MA) initiated by dibenzoyl peroxide (DBP), which is reflected by a significant increase in the polar component of the surface free energy. MA and DBP concentrations of 3 wt % each are sufficient for significant modification of the polarity of the wax. FTIR spectra confirm the presence of anhydride groups on the wax chains, while gel permeation chromatograms show the development of a low molecular

weight peak, which may be indicative of wax degradation. The grafting of wax by MA decreases the specific enthalpy of melting, as determined through differential scanning calorimetry. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 662–668, 2004

Key words: Fischer-Tropsch wax; grafting; maleic anhydride; polarity; differential scanning calorimetry (DSC); FT-IR; functionalization of polymers

INTRODUCTION

Paraffin waxes (Fischer-Tropsch synthesis) are aliphatic hydrocarbons consisting of straight or branched carbon chains. They are white, translucent, tasteless, and odorless solids consisting of a mixture of solid hydrocarbons of high molecular weight. Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odor and color. They are combustible and have good dielectric properties. They are used for preparation of candles, paper coating, protective sealant for food products and beverages, glass-cleaning preparation, hot-melt carpet backing, biodegradable mulch, lubricants, stoppers for acid bottles, electrical insulation, and others.¹

Waxes and polymers, particularly polyolefines as low-energy substances, have low surface free energy values.² The introduction of specific polar groups onto polymer chains through chemical modification leads to the improvement of physical interactions such as hydrogen bonds, van der Waals forces or dipolar interactions.³ This is reflected in higher values of surface energy, as well as in mechanical work of adhesion to more polar substrates.

The untreated paraffins and polyolefins possess poorer wettability, because of their low polarity and low adhesives properties,⁴ than the more polar sub-

strates, which restricts its use in several technologically important fields. These drawbacks can be overcome by graft polymerization of polyolefins⁵ or by adding more polar low or high molecular weight additives to the polymer melt.^{6,7} In fact, a small percentage of functionality can dramatically increase the surface energy and the adhesive properties of polyolefins. Grafting of polyolefins by monomers containing polar functional groups is a highly efficient means of increasing the surface free energy, as well as of regulating their adhesive interaction with different solid surfaces, including metals.^{8,9} Grafting has advantages over other methods of modification of polymers, among others the controlled introduction of grafted chains without changing the bulk properties. In the case of polyolefins, it is usually induced by a free radical initiator, but ionically initiated processes have also been used.^{10–13}

Nonradiation induced chemical modifications of polyolefins have been even more diverse. They include oxidation, reduction, substitution, elimination, cyclization, and addition reactions.^{14–17} The free radical polymerization using organic peroxides such as benzoyl peroxide is the most widely used method for the synthesis of grafted polymers, because the process is relatively simple. The synthesis of polyolefin graft copolymers by reactive extrusion is a similar method for enhancement of its wettability and adhesive properties.^{18,19}

For grafting of polyolefins, i.e., polyethylene, grafting and crosslinking in the melt are very important and are characterized by the formation of gels or

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partially insoluble products.²⁰ Moreover, the melt viscosity will be higher for grafted polyolefins as a consequence of the specific interactions between the introduced polar groups.²¹

Grafted waxes are also used in many practical applications. For example, wax-graft copolymer compounds are useful as components in polishes and in carbon paper inks. They are prepared by graft polymerization of vinyl compounds onto microcrystalline or Fischer-Tropsch waxes in the presence of a free-radical catalyst.²² Among other examples of the utilization of waxes modified with maleic anhydride (MA) belong wax waterproofing compounds²³ and different mixtures for the preparation of electrostatographic toners.²⁴

EXPERIMENTAL

The samples were prepared by mechanically mixing a hard Fischer-Tropsch wax (supplied by Schumann-Sasol in South Africa, average molecular weight 800 g/mol⁻¹, melting point 90°C, density 0.94 g cm⁻³ at 25°C), MA, and dibenzoyl peroxide (DBP) (both supplied by Sigma-Aldrich). This was followed by heating the mixture in an oil bath at 140°C for 10 min in nitrogen atmosphere, cooling down and grinding of the sample, washing in boiling water to dissolve unreacted MA, if any, followed by filtering and drying in an oven at 50°C.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-7 thermal analyzer in nitrogen atmosphere. Samples were heated from 25 to 140°C at a heating rate of 10°C min⁻¹ and then cooled at the same rate. Thermal properties, such as melting and crystallization temperatures and enthalpy, were determined from the second scan.

The surface free energy of the waxes was determined by measurement of contact angles θ of various testing liquids [twice distilled water, glycerine p.a., formamide p.a., 1-chloronaphthalene (Merck, SRN), methylene iodide p.a. (Fluka, SRN), thiodiglycol, ethyl-2-aminobenzoate p.a., ethylene glycol p.a., (Serva, SRN)], having different polarities, with a Contact Angle Meter (Zeiss, Germany). The relation $\theta = f(t)$ was extrapolated to $t = 0$ and the surface free energy and its polar component were evaluated by using a computer program based on a least squares method by minimizing equation (1):²⁵

$$\frac{(1 + \cos\theta) \times (\gamma_{LV}^d + \gamma_{LV}^p)}{2} = (\gamma_{LV}^d \times \gamma_s^d)^{1/2} + (\gamma_{LV}^p \times \gamma_s^p)^{1/2} \quad (1)$$

where θ (deg) is the contact angle, γ_{LV}^d , γ_{LV}^p (mJ/m²) are the polar and dispersive components of the surface free energy of the testing liquid, γ_s^p , γ_s^d (mJ/m²) are the

TABLE I
Total Surface Free Energy, Its Polar and Dispersive Components, and the Polar Fraction of Grafted Wax^a

Sample	γ (mJ/m ²)	γ^p (mJ/m ²)	γ^d (mJ/m ²)	x_s^p
100/0/0	29.0	0.3	28.7	0.01
98/1/1	32.4	0.6	31.8	0.02
96/3/1	34.2	0.9	33.3	0.03
94/5/1	38.4	2.8	35.6	0.07
89/10/1	36.2	2.4	33.8	0.07
96/1/3	33.3	0.5	32.8	0.02
94/3/3	36.9	3.8	33.1	0.1
92/5/3	35.6	3.9	32.6	0.1
87/10/3	35.9	3.4	32.5	0.1
94/1/5	34.3	1.7	32.6	0.05
92/3/5	35.6	3.5	32.1	0.1
90/5/5	36.3	3.4	32.9	0.1
85/10/5	36.5	3.5	33.0	0.1

γ , total surface free energy; γ^p , polar component; γ^d , dispersive component; x_s^p , polar fraction.

^a Notation $x/y/z$, wax/MA/DBP m/m ratios.

polar and dispersive components of the surface energy of the polymer, and

$$\gamma_s^{\text{total}} = \gamma_s^p + \gamma_s^d \quad (2)$$

where γ_s^{total} (mJ/m²) is the total surface energy of the polymer. It holds for the polar fraction x_s^p :

$$x_s^p = \frac{\gamma_s^p}{\gamma_s^{\text{total}}} \quad (3)$$

Infrared analyses were performed on a Nicolet Impact 410 FTIR spectrometer connected to a photoacoustic cell. A carbon disk was used to obtain a baseline under helium atmosphere. A resolution of 8 cm⁻¹, a scan range of 4,000–500 cm⁻¹, and a total of 200 scans per analysis were used.

Gel permeation chromatographic (GPC) analyses were performed on a Waters 150-C chromatograph. The column and injector compartment temperatures were 120°C, while the pump temperature was 55°C. Xylene was used as solvent, with an injection volume of 100 mL and a flow rate of 0.5 mL min⁻¹.

RESULTS AND DISCUSSION

Surface free energy measurement

The measurements of the surface free energy, its polar and dispersive components, and the polar fraction are summarized in Table I. Here it can be seen that the grafting of MA by DBP improves the polarity of the wax in all cases, especially the polar component of the surface free energy and the polar fraction. This effect is very significant for the compositions of wax containing 3, 5, and 10 wt % of MA and 3 and 5 wt % of DBP.

TABLE II
Parameters Obtained from DSC Measurements of Grafted Wax^a

Sample	$T_{o,m}$ (°C)	$T_{p,m} = T_m$ (°C)	ΔH_m (J/g ¹)	$T_{a,c} = T_c$ (°C)	$T_{p,c}$ (°C)	ΔH_c (J/g ¹)
100/0/0	60.1	77.2	213.1	95.2	67.1	211.2
99/0/1	54.6	72.0	173.3	91.5	63.6	178.9
97/0/3	54.6	71.9	168.4	90.8	63.5	175.1
95/0/5	54.4	70.7	136.5	89.7	63.3	148.1
98/1/1	58.7	76.0	207.0	94.6	68.7	222.1
96/1/3	58.3	75.5	163.5	94.3	69.7	182.8
94/1/5	56.9	78.5	151.2	93.5	67.9	170.0
96/3/1	58.8	74.7	204.4	95.1	68.5	221.5
94/3/3	58.4	75.0	156.4	93.6	68.8	170.6
92/3/5	59.1	80.0	146.4	93.3	70.5	170.8
94/5/1	58.1	75.1	164.3	94.9	69.8	172.7
92/5/3	60.8	81.4	186.4	93.6	70.9	199.5
90/5/5	59.9	81.2	194.6	93.1	71.2	205.2
89/10/1	61.1	70.7	174.2	95.1	69.3	194.2
87/10/3	59.0	76.9	177.7	93.8	72.0	163.3
85/10/5	58.8	76.7	135.5	92.5	70.7	151.3

^a T, temperature; ΔH , specific enthalpy; m, melting; c, cooling; o, onset; p, peak. Notation x/y/z, wax/MA/DBP m/m ratios.

It is evident that concentrations of MA and DBP of 3 wt % each are sufficient for significant modification of the polarity of wax. Further increase in the concentration of MA and DBP in wax does not lead to a further increase in polarity.

The surface free energy of pure nonpolar polyethylene is influenced by the degree of crystallinity, antistatics, additives during the polymerization process, etc. Grafting of polyolefin with MA leads to an introduction of polar functionalities, which significantly improve its surface free energy and mainly its polar component and polar fraction.²⁶ These experimental results were confirmed in our previous papers.^{7,27}

Differential scanning calorimetry

Differential scanning calorimetry was employed to check the influence of grafting on the change in melting as well as crystallization temperatures and enthalpies. The results obtained from DSC analyses are summarized in Table II. The concentration of DBP is too low to form a space network (gel), but it is enough to form locally crosslinked or branched domains.^{28,29} This fact is confirmed by GPC, where an increase in molecular weight with an increase in DBP was observed.

Two parallel reactions are possible during the heating of wax/MA/DBP mixtures. Peroxide enables grafting of MA onto wax chains, but also crosslinks or branches wax chains. A decrease in $T_{o,m}$, T_m , and enthalpy (ΔH_m being a measure of the degree of crystallinity) of wax (in the absence of MA) with an increase in DCP is clearly observed. It therefore seems as if crosslinking reduces the wax crystallinity. Crosslinks play the role of defect centers, which im-

pede the folding of macromolecular chains, and thus decrease the sizes of the lamellar crystals.³⁰ The reduction of lamellar thickness of crystallites leads to a decrease in T_m . The actual values of T_m for a given sample of crosslinked polyethylene or wax depend on the initial crystallinity of the material, the temperature at which crosslinking is conducted, as well as the conditions of crystallization before a measurement. Grafting of MA onto wax chains also decreases the specific enthalpy of melting, since MA side chains also play the role of defect centers. Onset and peak temperatures of melting, however, seem to increase with increasing MA content. This is probably the result of stronger interaction between the wax chains in the presence of polar anhydride groups.

Gel permeation chromatography

Figure 1 shows the GPC chromatograms of the different MA/DBP-treated wax samples. The differences in size and intensity of the peak at a retention time of about 15 min show no trend and may be attributed to (i) differences in concentration of the analyzed solutions and (ii) crosslinking and/or branching of the wax chains giving rise to reduced peak sizes of the main wax peak. What is, however, interesting is the development of a second peak at a retention time of about 30 min, especially for samples treated with high concentrations of MA. It cannot be the result of unreacted MA, because MA elution occurs at about 40 min under our analysis conditions, and the sample treatment before analysis was such that no unreacted MA should have been found in the samples. It seems as if MA grafting causes degradation and the development of a lower molar mass wax fraction.

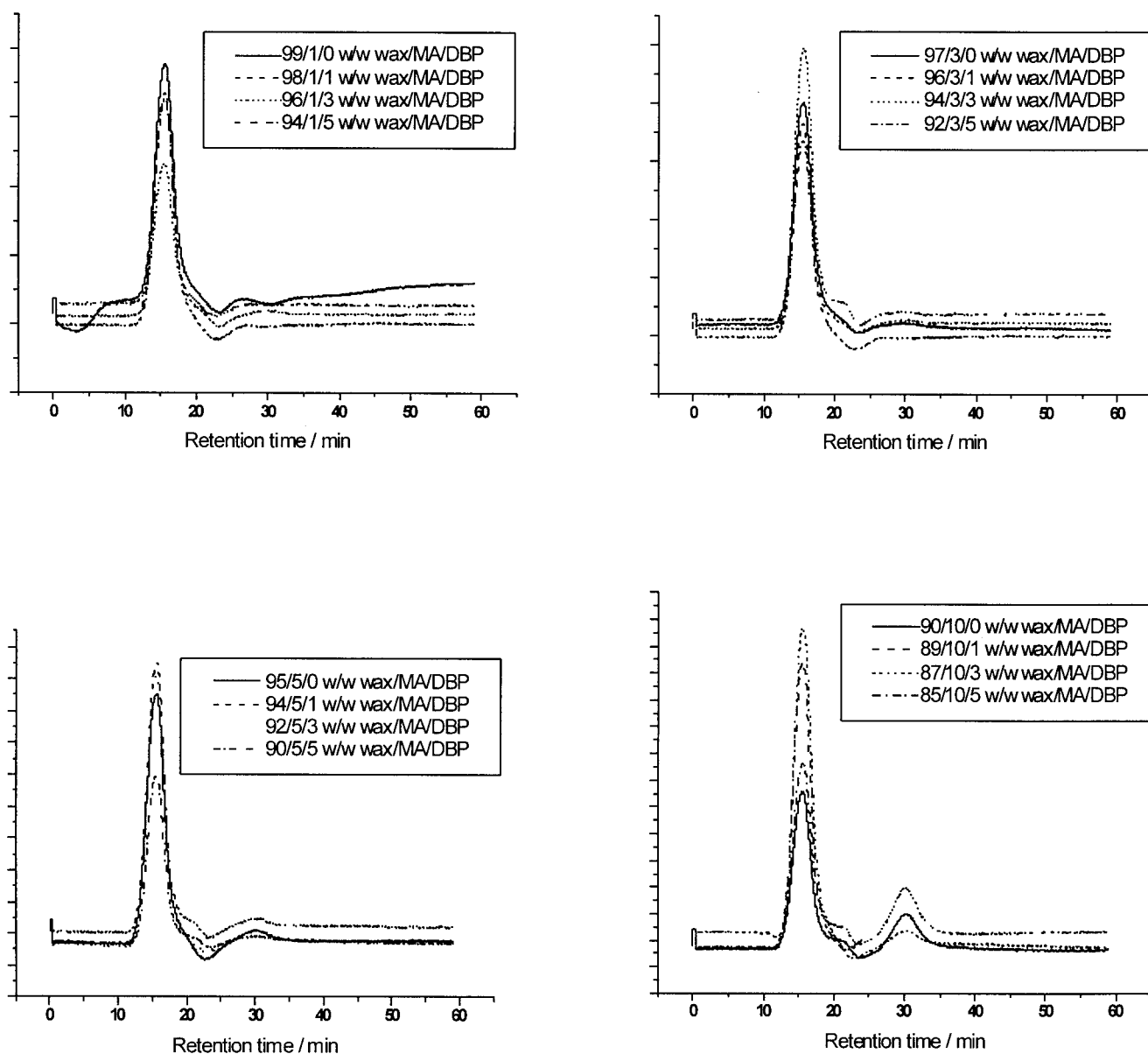


Figure 1 Gel permeation chromatograms of wax samples treated with different combinations of maleic anhydride and dibenzoyl peroxide.

FTIR spectroscopy

That grafting does occur is clear from the FTIR spectra (Figs. 2 and 3) where an anhydride band develops at about $1,715\text{ cm}^{-1}$ with increasing MA concentration in the samples at constant DBP concentration (Fig. 2) and with increasing DBP concentration at constant MA concentration (Fig. 3). Grafting seems to be most effective at an MA concentration of 10 wt % and DBP concentrations of 3 or 5 wt %.

CONCLUSION

The grafting of MA by DBP improves the polarity of the wax and is reflected by an increase in the polar

component of the surface free energy, as well as its polar fraction. Concentrations of MA and DBP of 3 wt % each are sufficient for significant modification of the polarity of the wax. Further increase in the concentrations of MA and DBP did not lead to a significant additional increase in polarity.

A decrease in $T_{o,m}$, T_m , and enthalpy of the wax in the absence of MA with an increase in DCP was clearly observed. The reduction of lamellar thickness of crystallites leads to a decrease in T_m . The grafting of wax by MA decreases the specific enthalpy of melting, since MA side chains play the role of defect centers, and increases the melting temperature.

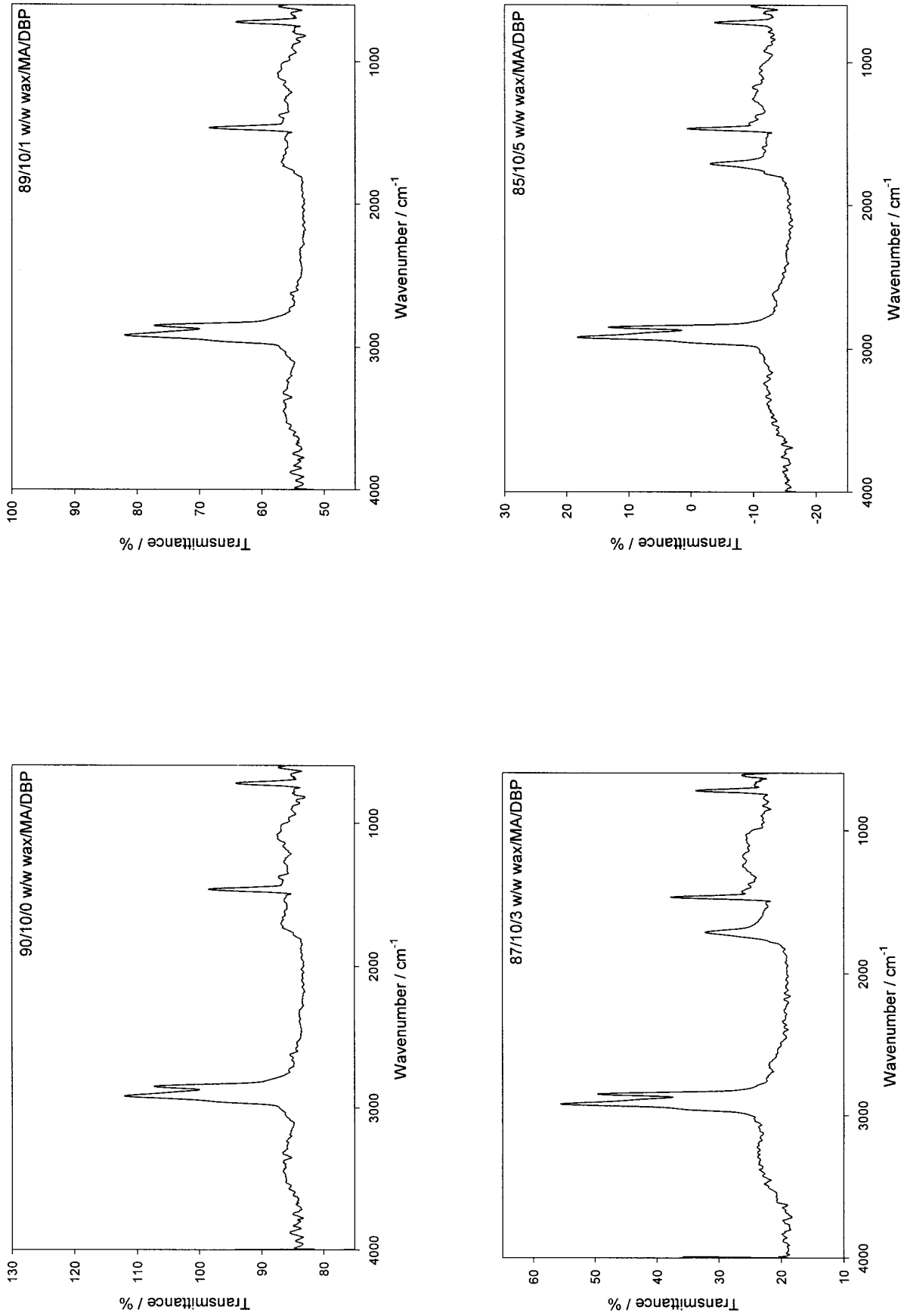


Figure 2 FTIR spectra of wax samples treated with 10 wt % maleic anhydride and different concentrations dibenzoyl peroxide.

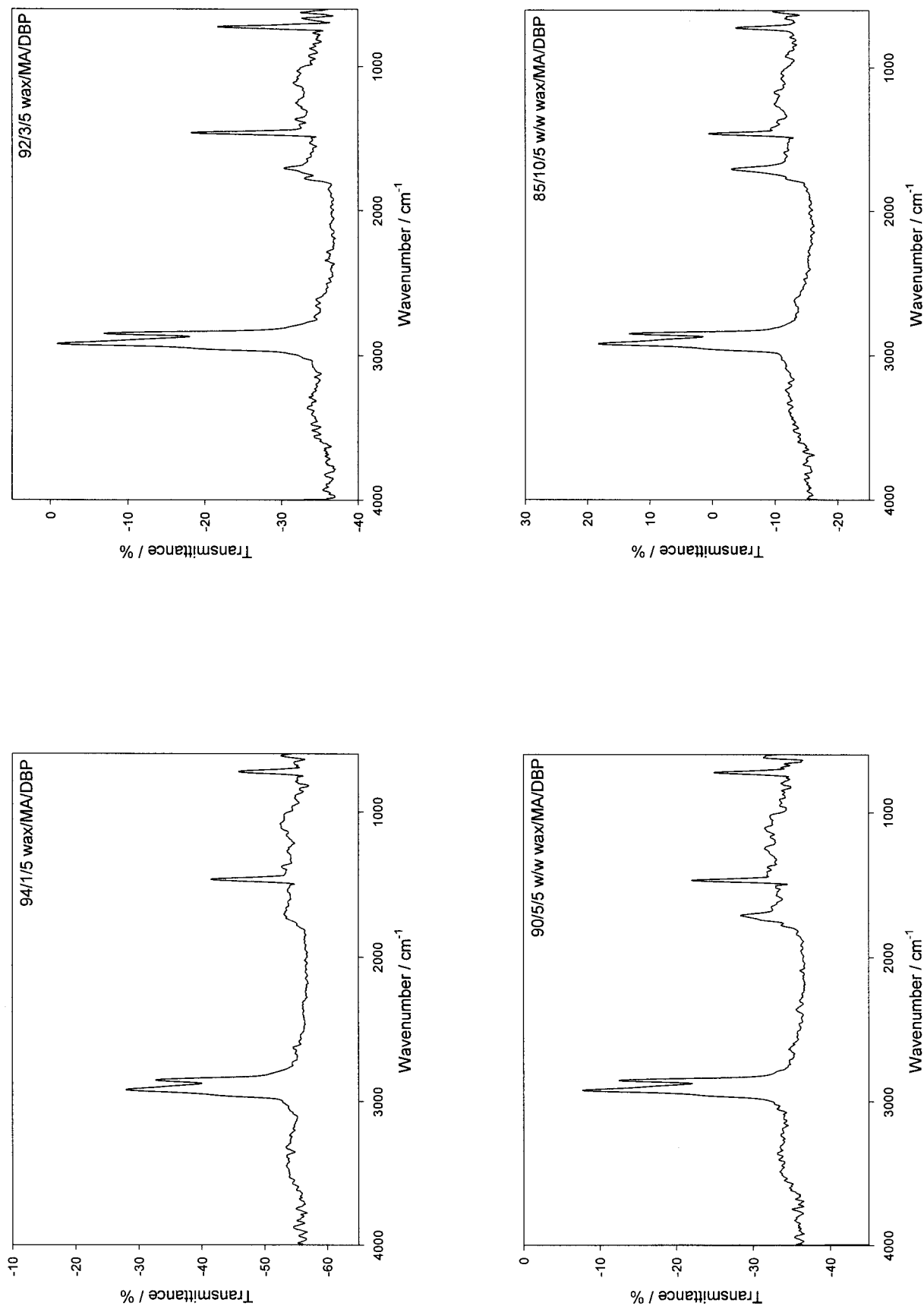


Figure 3 FTIR spectra of wax samples treated with 5 wt % dibenzoyl peroxide and different concentrations maleic anhydride.

Grafting of MA onto wax chains is confirmed by the FTIR band that develops at about $1,715\text{ cm}^{-1}$ with increasing MA concentration in the samples at constant DBP concentration and with increasing DBP concentration at constant MA concentration. Grafting seems to be most effective at an MA concentration of 10 wt % and DBP concentrations of 3 or 5 wt %.

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