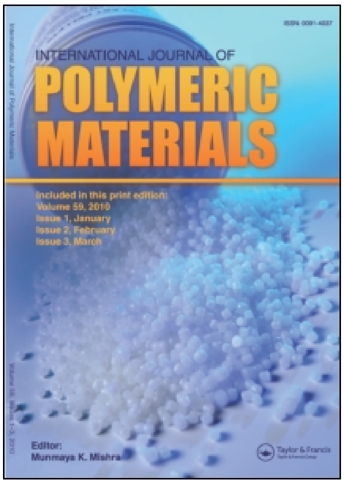

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Suman, Michele(2001) 'Identification of Hydrocarbon Components Generated by Transformation Processing of Cast Polypropylene Employed for Combining with Other Plastic Films', International Journal of Polymeric Materials, 49: 1, 91 — 100

To link to this Article: DOI: 10.1080/00914030108035869

URL: http://dx.doi.org/10.1080/00914030108035869

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 91–100
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Identification of Hydrocarbon Components Generated by Transformation Processing of Cast Polypropylene Employed for Combining with Other Plastic Films

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(Received 3 January 2000; In final form 6 January 2000)

In many packaging applications, next to the traditional custom of bi-oriented polypropylene (BOPP) there is an increasing use of polypropylene easily extrudable in film form, commonly known as cast polypropylene (CPP). More precisely, the combined structures BOPP-CPP unite the good barrier properties of the BOPP with those of tenacious weldability and tear resistance typical of the CPP.

The operational conditions of extrusion and the raw materials adopt for forming these two kinds of film are not identical: sudden changes in temperature and the contemporaneous presence of propylene-ethylene units involve the formation of characteristic by-products of paraffinic nature (*e.g.*, 2,3,4-trimethyl-pentane) and olefin nature (*e.g.*, 2,4-dimethyl-1-heptene) in the CPP.

They appear then like characteristics "markers" of CPP film destined to have a welding layer function; by the way their concentrations are very low (less than 0,5 mg/m^2) and their effect is practically absent in terms of anomalous odors that may be found on the packing.

Keywords: Polypropylene; Poly(propylene-co-ethylene); Barrier properties; Degradation products

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INTRODUCTION

Cast polypropylene (CPP) is a material that currently finds application in those packings in which an high resistance to tear is required in order to guarantee a good re-closure of the packages.

Relative to low density polyethylene (LDPE), the CPP shows a better transparency (important when the visibility of the contained substance inside the packages is desirable) and the value of the tear resistance is about halved (at comparable thickness), yet decidedly higher than bi-oriented polypropylene (BOPP) [1].

In the CPP the barrier properties to water vapor and to gases are higher relative to LDPE; but they are usually insufficient, especially for preserving alimentary commodities (food stuffs) with long shelf life. For this reason CPP is commonly combined as a welding layer (sealing temperature around 115°C) with other films (above all with BOPP) that could serve to compensate the deficit in barrier properties.

The conditions of thermal treatment applied during the fusion extrusion of the two kinds of films considered here (CPP and BOPP) are different.

The production technology of CPP employs an extrusion of the fused granule (with temperatures that reach 240–260°C) across a slot with a controlled thickness, followed by an abrupt stabilization on cooled cylinder or in a water bath; BOPP, however, undergoes a process of very slow and controlled cooling [2], so as to delay excessive shrinking and promote the following orientation mechanics process.

In fact, considering that after the extrusion in sheet it must be then bi-axially oriented, BOPP is made as a film with a thickness of about 40 times the value of the final thickness. For example, to obtain a film with a final thickness of 25 μm, it is necessary to extrude an initial thickness of 1000 μm: as a consequence the cooling time is very long and the changes in temperature are gradual.

Commonly then the raw material granules used for making CPP film constitute of macromolecular chains shorter and with a lower molecular weight (therefore with a higher Melt Index) compared to those employed for BOPP film.

Additionally in the case of CPP film, the polymeric material granules are not made of pure polypropylene, but instead of a random polypropylene-polyethylene copolymer with around 4 weight%

polyethylene, which guarantees a tenacious welding already at low temperatures (~120°C).

The objective of this study has been to evaluate how the effect of a large "thermal stress", of shorter polymeric chains typified by alternation of propylene\ethylene units, translates in the CPP film to the formation of by-products which are absent in the case of BOPP.

EXPERIMENTAL PART

Materials Employed

- Cast polypropylene (CPP), thickness 25 μm
- Bi-axially-oriented Polypropylene (BOPP), thickness 20 μm
- Combined film BOPP 20 μm + PPcast 25 μm printed on the internal side of the BOPP.

Gas Chromatographic Analysis (Static Head Space)

The analysis of the films consisted of sampling 50 cm^2 of film surface and inserting it in a 20 ml vial closed with a PTFE-rubber septum and an aluminum cork. This vial was then placed in a 120°C thermostatic oven for 30 minutes. Afterward 1 ml of its head space has been injected by means of a "Dani HSS 86.50" autosampler directly in the injection chamber of the gas chromatograph ("Fisons Mega HRGC 5300" with capillary column "Chrompack CP-WAX 52 CB 50 × 0,32 mm").

The method follows the principal steps of the UNI-standard [3].

The detector was a FID constantly maintained at 250°C; the carrier gas used was helium.

The quantitative determinations have been performed through comparison of the areas obtained from calibrating solutions with known quantities of the pure solvents, injecting them in a sealed vial.

GC-MS Analysis (with Criofocusing-dynamic Head Space)

In this case the sealed vial has been filled with 50 cm^2 of film and then it was heated in an oven at 105°C for 15 minutes, after that the vial was connected to the injection system.

This system consists of two needles of which the longer one serves to pump helium that washes the inside atmosphere of the vial: the shorter one carries then the gas toward a capillary cooled trap with liquid nitrogen (up to $-100°C$) that allows the organic compounds to be criofocused for a period of up to 180 seconds. The trap is then quickly heated up to 240°C and so is able to release into the column the substances that have been previously concentrated.

The used column is a "MEGA JXR": film thickness 3,5 μm – length 50 m – internal diameter 0,32 mm – column material methyl-siloxane.

The detector is a mass selector with an electronic impact energy of 70 eV; it has operated with scan conditions in total ionic current.

Olfactory Analysis

This method has been developed in-house, however it follows the principal steps of the UNI-standard [4].

Film samples have been analyzed (with a surface of 1 dm^2) in terms of odor by setting them in a heated flask at pre-set temperature and time.

At the same time it has been prepared a "blank", *i.e.*, an empty flask, closed and conditioned under the same conditions anticipated for the other samples.

After the conditioning, the flasks were brought to ambient temperature and each panelist was asked to smell the content of each encoded sample flask, comparing it with the "blank" flask and finally assigning a judgment according to the following classification:

0: no noticeable difference of odor
1: hardly noticeable difference of odor
2: weak but definite difference of odor
3: strong difference of odor
4: very strong difference of odor.

RESULTS

Gas Chromatographic Analysis

The chromatograms obtained from the analysis of the BOPP before printing and combining with CPP, produce patterns absolutely barren of relevant components.

A different statement has to be made for the CPP, whose pattern is characterized by traces associated with at least 4-5 different kinds of molecules released from the polymeric material.

The same traces can also be found in the chromatograms obtained from the finished combined and printed film (BOPP reverse printed + CPP) and they do not belong to any solvent employed in the printing process. These results are presented in Table I.

Olfactory Analysis and Information on the Characterized Compounds

The results obtained from the panel group have not identified perceptible differences among the CPP and the combined printed film. Moreover, both has been judged as having very low levels of odor.

In fact, on a classification with increasing values from 1 to 5, the maximum score achieved is 2, and that in the case of only one member of the panel group: see Table II.

TABLE I Quantitative data of the principal compounds identified in gas chromatographic analysis performed on the films (for the known compounds amounts are expressed in milligrams in a film sample with an area of $1\,m^2$; for the unknown compounds values reported below are referred to their peak-area in the chromatogram)

Compounds	*Units*	*BOPP*	*CPP*	*BOPP + CPP*
Hexane	mg/m^2	/	/	0,15
Cyclohexane	mg/m^2	/	/	0,1
Acetone	mg/m^2	/	/	0,15
Ethyl acetate	mg/m^2	/	/	5,5
Isopropyl acetate	mg/m^2	/	/	0,5
Isopropyl alcohol	mg/m^2	/	/	0,5
Ethanol	mg/m^2	/	/	1
Not identified 1	Area units	/	3216	4195
Not identified 2	Area units	/	9275	11168
Not identified 3	Area units	/	1277	1240
Not identified 4	Area units	/	1992	2055
Not identified 5	Area units	/	1993	2114

TABLE II (Olfactory judgments of each member of the panel group according to the 0–4 classification previously reported)

FILM	*Panel member* 1	*Panel member* 2	*Panel member* 3	*Panel member* 4	*Panel member* 5	*Panel medium*	*Standard deviation*
CPP	0	0	1	2	1	0,8	0,74
BOPP + CPP	0	0	1	1	1	0,6	0,49

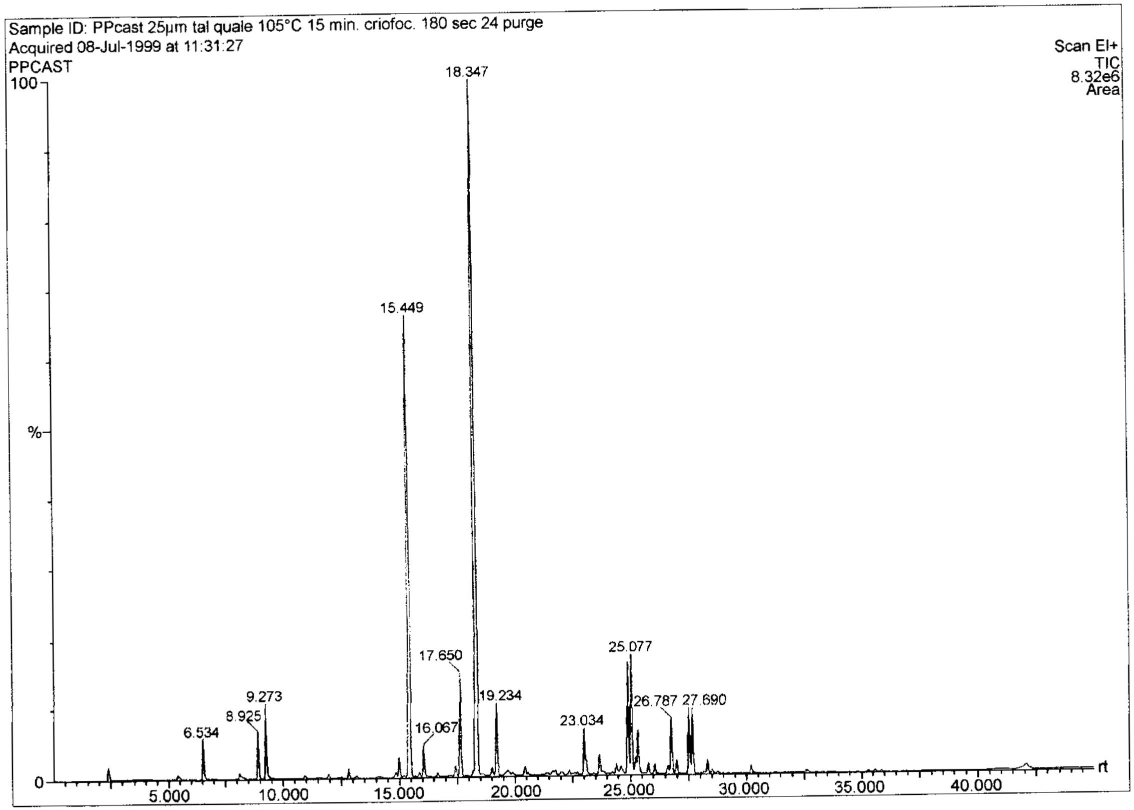


FIGURE 1 GC-MS chromatogram obtained on CPP 25 µm.

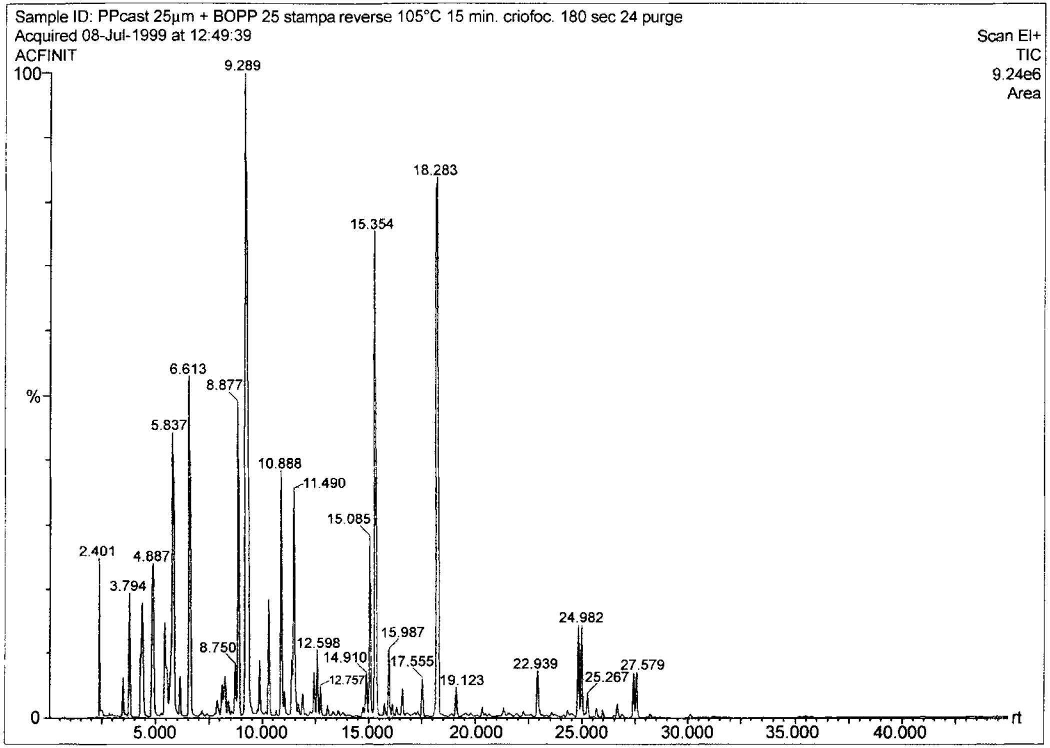


FIGURE 2 GC-MS chromatogram obtained on BOPP 25 µm + PPcast 25 µm.

TABLE III "Semiquantitative values" of the principal compounds identified in GC-MS analysis performed on the films (values expressed in mg/m^2 where not otherwise indicated; "/" means lower than 0,01 mg/m^2)

Compounds	*BOPP*	*CPP*	*BOPP + CPP*
2-methyl-1-pentene	/	< 0,1	< 0,1
Ethyl acetate	~0,3	< 0,1	5,5
2,3,4-trimethyl-pentane	/	~0,2	~0,2
2,5-dimethyl-1-hexene	/	< 0,05	< 0,05
Octane	/	< 0,05	< 0,05
2,4-dimethyl-1-heptene	/	~0,4	~0,4
"total area of branched hydrocarbons"	/	$1,8 \cdot 10^7$area units	$2,2 \cdot 10^7$area units

GC-MS Analysis

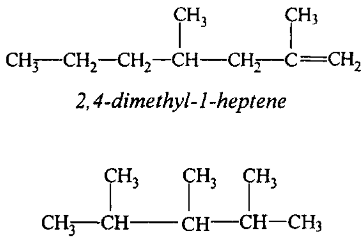
Samples of film obtained from BOPP has confirmed the absence of compounds that can be released from the film. There is only the presence (in amounts lower than 0,3 mg/m^2) of ethyl-acetate, an impurity probably present in the production environment of the film.

However, in the case of the CPP, the criofocusing in the injection phase of the GC and the following analysis with mass spectrometer produced very useful information on the compounds that the simple gas chromatographic analysis with FID detector had already indicated as unknown peaks.

The same substances, obviously associated with normal levels of residual solvents due to the printing process, were then found also in the combined printed BOPP-CPP film. These observations are shown in the chromatograms in Figures 1 and 2, and the results in Table III: the "semiquantitative evaluations" reported are based easily on comparisons of the integrated areas of the peaks with the corresponding areas relative to well known amounts of heptane separately injected, and analyzed under the same operational conditions.

CONCLUSIONS

The investigation has shown how (in difference to what happens for Bi-oriented Polypropylene – BOPP –) the extrusion technology of Cast



2,4-dimethyl-1-heptene

2,3,4-trimethyl-pentane

FIGURE 3 Main by-products identified in cast polypropylene film.

Polypropylene – CPP – involves thermal stress that, associate with the presence of more disordered macromolecular chains (which contain either polypropylene units or ethylene units) determines the formation of some characteristic decomposition by-products.

They probably originate initially from tertiary stable radicals that could be produced during the high temperature stages that precede the abrupt cooling of the extruded film; two compounds present at high levels has been characterized: 2,4-*dimethyl-heptene* and 2,3,4-*trimethyl-pentane*. The formation mechanism of these compounds remains to be clarified in detail but it can be noticed from Figure 3 that the 2,4-dimethyl-1-heptene structure could be "glimpsed" in the polymeric chain formed from propylene and ethylene; however, it appears that a more complex explanation is needed to rationalize the presence of 2,3,4-trimethyl-pentane.

2,4-dimethyl-heptene and 2,3,4-trimethyl-pentane are still obviously found in the combined final film (reverse printed BOPP + adhesive + CPP) that is commonly employed in multifarious packaging applications, either alimentary or not.

Anyway, certainly their concentration (that had been estimated at values lower than 0,5 mg/m^2) do not arouse worry in terms of toxicity (moreover, a very similar compound, 2,6-dimethyl-5-heptene, is currently used as an aroma [5] in ice creams, non-alcoholic drinks, *etc.*); above all they had not resulted in perceptible (to the sensorial analysis) unpleasant odors neither on the CPP film nor on the combined final BOPP-CPP film.

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