

LAMINATION OF POLYMER FILMS BY BULK SURFACE PHOTOGRAFTING
PROCESS AND PROPERTIES

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Abstract A new process for lamination of polymer films by “bulk surface photografting” has been developed. The chemical component of the invention is that the curing of reactive solution between two substrates is initiated by the surface free radicals produced by aromatic ketones and surface-hydrogen of substrates. Using the new approach, two or more polymer films are bonded together by a grafted polymer network which is grafted to adjacent substrate surfaces. The technique has been applied to film substrates of different polymers such as polyolefins, polyesters, and polyamides which have abstractable hydrogens at the surface. The photolaminated film composites containing carrier films and an intermediate functional film of low permeability give strong laminates with high barrier properties, e.g. for oxygen and air.

Keywords Photografting, Lamination, Surface graft polymerization, Photolamination

INTRODUCTION

Photoinitiated modification of polymers has been developed in our laboratories in three main directions: photoinitiated crosslinking, surface photografting and photolamination of polymer films^[1].

Photocrosslinking has mainly been studied for polyethylene and a continuous rapid process for photocrosslinking on line with an extruder has been designed^[2].

Surface photografting has been developed for various commercial polymers and successfully applied to film, filaments and yarn^[3].

Photolamination of thin films is our most recent application and comprises a combination of surface photografting and bulk photopolymerization, i.e. bulk surface photografting^[4].

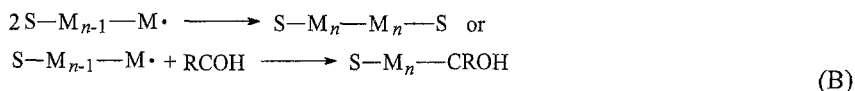
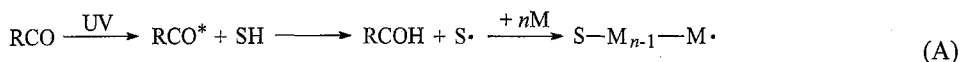


Fig. 1 Basic photoinitiated reactions in photomodification of polymers: initiation and propagation (A) and alternative terminations (B)

The three photoprocesses are related and based on the same radical reaction mechanism for initiation. The reaction system has three main components: a polymer substrate (SH), a hydrogen abstracting photoinitiator

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Plenary lecture at the International Conference on New Trends in Functional Polymers, May 8th–13th, 2000, Huangshan, China

Received September 1, 2000

(RCO) and a vinyl monomer (M) (Fig. 1). When the system is irradiated with near ultraviolet light (250–400 nm) the initiator (usually an aromatic ketone) absorbs UV light and is excited to a triplet state which abstracts hydrogen from the substrate. The surface radicals formed initiate polymerization by adding monomer and form grafted polymer. The chains are terminated by radical combination either with other growing chain ends or with ketyl radicals from the initiator (Fig. 2)

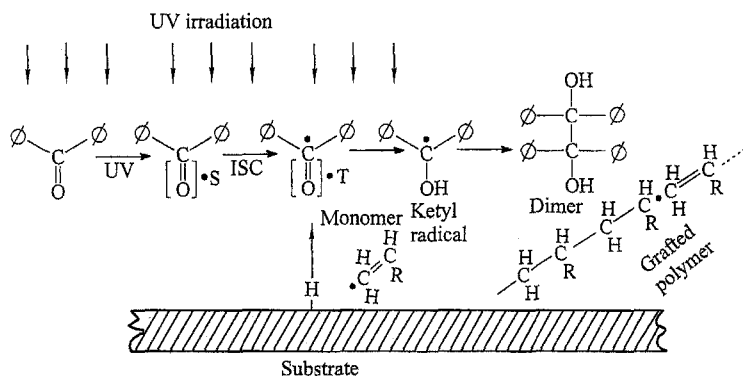


Fig. 2 Schematic picture of the basic reactions in surface photografting of a vinyl monomer, e.g. acrylic acid with benzophenone as initiator

In photocrosslinking no monomer is required. The excited initiator in triplet state abstracts hydrogen from the substrate chains and the radicals formed crosslink the polymer by radical combination. A small amount of a reactive multifunctional monomer may be added to increase the rate of crosslinking.

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Experimental

In photolamination the reactions occur between two substrate films, of which the top film must be transparent to the active UV irradiation (Fig. 3). The reactive composition of monomer and initiator forms a thin layer (5–15 μm) between the top and the bottom films. Good wetting is important. The first step of the reaction is surface photografting. Short grafted chains grow from both inner surfaces of the laminate (Fig. 4a). When the UV irradiation continues the excited initiator abstracts hydrogen from the grafted chains which initiates branching of the chains (Fig. 4b). The reaction continues until initiator and monomer are consumed and the space between the two substrate films is filled with a polymer network which is connected to the two surfaces with main valence bonds (Fig. 4c). Some pairs of growing chain ends may be terminated by radical combination which forms the polymer network. By adding a multifunctional vinyl monomer to the reactive composition, the crosslinking is enhanced which increases the lamination strength.

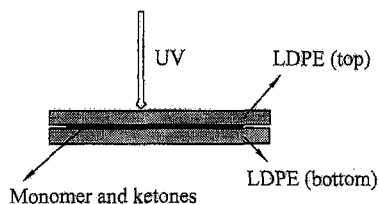


Fig. 3 Device for photolamination of two LDPE films with an intermediate reactive layer by "bulk surface photografting"

For a reactive vinyl monomer like acrylic acid, formation of grafted polymer is favored^[5]. Only minor amounts of homopolymer are formed because the ethylenic hydrogens of the monomer have high bond strength (106 kcal/mole). In the grafted chains formed every second carbon has a tertiary bonded hydrogen which has low

bond strength (93 kcal/mol) and is easily abstracted. This favors branching of the chains by secondary grafting (Fig. 5).

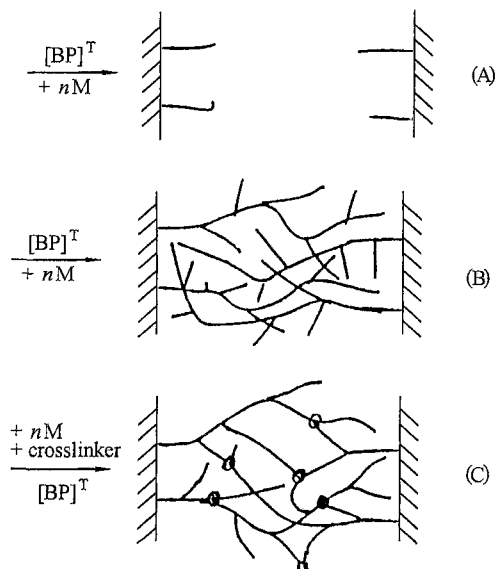


Fig. 4 (A), (B), (C) formation of laminate by “bulk surface photografting” between two polymer film substrates

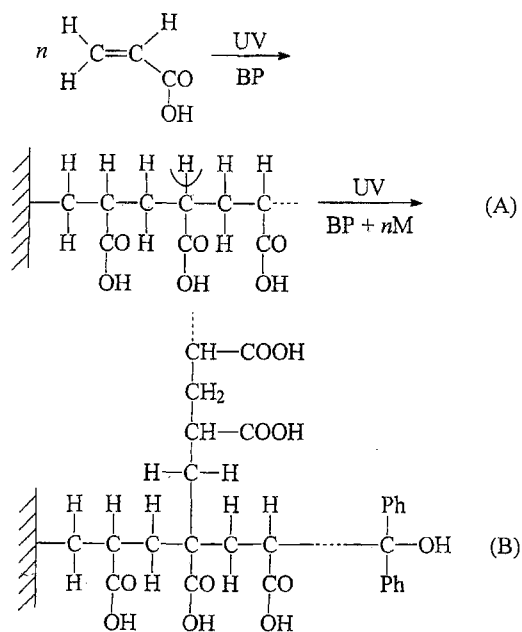


Fig. 5 Mechanism of formation of secondary grafted chains

In photolamination the reactive layer is enclosed between two substrate films and is not accessible to the air. Outer atmosphere of nitrogen is therefore not required in photolamination experiments.

After photografting the reactive layer of the laminate has higher strength than the commercial thermoplastic substrate films as measured by T-peel tests of the laminates (Table 1), the failure site is in the substrate films. Of the film materials tested, increasing cohesive strength is measured in the order LDPE < PP < PET < Nylon-66 as derived from Table I^[5].

Table 1. T-peel strength of different photografted laminates ^a

Laminate (thickness mm)	UV irradiation time (s)	Failure side (Broke)	Peel strength (Broke, N/m)
LDPE/LDPE (0.188//0.188)	25	LDPE	1050
PP/PP (0.1//0.1)	45	PP	2310
LDPE/PET (0.188//0.256)	15	LDPE	1050
PP/PET (0.1//0.256)	20	PP	1580
LDPE/Nylon-6 (0.188//0.12)	10	LDPE	1340

^a Reactive layer is acrylic acid with 5% benzophenone.

The cohesive strength of the substrate film is, however, affected by penetration of monomer and initiator into the bulk of the films during the irradiation^[6]. In experiments with two LDPE films (25 μ m) and a reactive layer of acrylic acid with 5 wt% benzophenone, surface photografting was found to occur on both sides of the substrate films. It was evidenced by contact angle measurements of a drop of water on the “inner” and the “outer”

surfaces of the top and bottom films (Fig. 6) and also verified by reflection FT-IR measurements. The grafting of the monomer in the bulk of substrate films may strengthen the film material by simultaneous crosslinking.

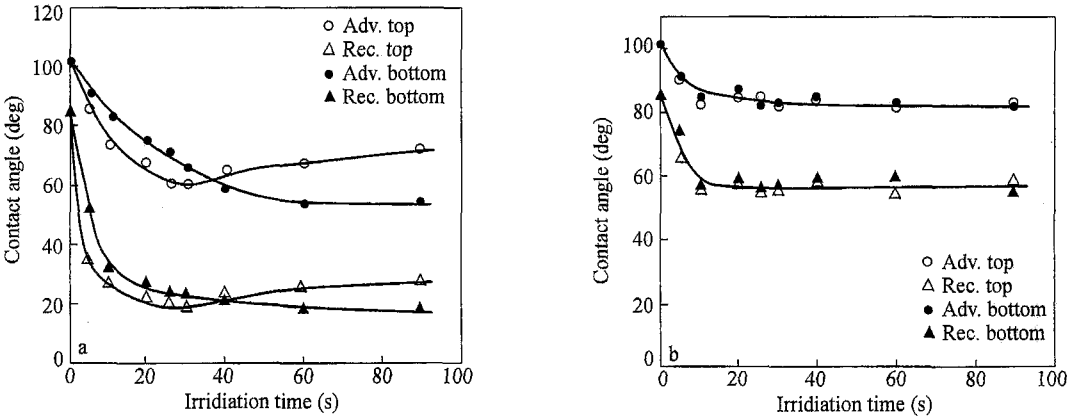


Fig. 6 Advancing and receding contact angle for photografted substrate films on the “inner” (A) and “outer” (B) surface

Photolamination has been applied to composite film packs of a strong supporting bottom film (e.g. polyethylene terephthalate, PET), an intermediate functional film with high barrier properties (e.g. polyvinyl alcohol, PVA) and a protective top film (e.g. low density polyethylene LDPE) (Fig. 7). A photoreactive layer (7 μm) decreases the rate of permeation of air and oxygen by a factor of 50–60 when applied between two LDPE films (63 μm). For the 3 film packs the barrier effect is much larger after photografting (Table 2) with a decrease of the permeation rate by a factor of about 10,000 for air and oxygen which is of commercial interest for industrial applications.

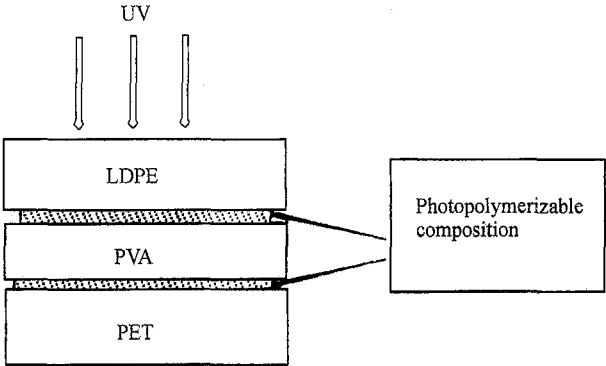


Fig. 7 Laminate of three films by “bulk surface photografting”

Table 2. Permeability to oxygen of photografted laminates of the carrier films of low density polyethylene (LDPE) and polyethylene terephthalate (PET) and the functional films of polyvinylidene chloride (PVDC) and polyvinyl alcohol (PVA) ^a

No.	Laminate: film samples	Thickness (μm)	Permeation rate P ($\text{mL O}_2/\text{m}^2 \text{ day}$)
BYL-2	LDPE//LDPE	63/63 (No grafting)	2097
BYB-10	LDPE//LDPE	63/12/63	1077
BYB-4	LDPE//PVDE//LDPE	63/8/10/8/63	78
BYB-8	LDPE//PVA//LDPE	63/7/12/7/63	0.1
BYB-7	LDPE//PVA//PET	63/12/12/12/125	0.1

^a The reactive layer // is acrylic acid and benzophenone (5 wt%).

Discussion

Lamination by “bulk surface photografting” is in principle a new process. Two or more polymer films are bonded together by a grafted polymer network containing main valence bonds. This means mechanically strong and permanent laminates. The process allows the lamination of different film materials as substrates, e.g. polyolefins, polyesters and polyamides, which have abstractable hydrogens available at the surface. In this way laminates can be produced containing carrier films and functional films combined giving very high barrier properties. The reactive layer is enclosed between the substrate films. Therefore, the photolamination is a simple process which does not require inert atmosphere during the UV irradiation.

CONCLUSIONS

A new process for lamination of polymer films by “bulk surface photografting” has been developed.

The photolamination involves formation of a bonding layer of a main valence polymer network which is grafted to adjacent substrate surfaces. The photolamination has been applied to film substrates of different polymers, e.g. polyolefin, polyesters and polyamides, having abstractable hydrogens at the surface. The photolaminated film composites containing carrier films and an intermediate functional film of low permeability give strong laminates with high barrier properties, e.g. for oxygen and air.

Acknowledgements The research work presented in this paper has been supported by grants and fellowships from the Knut and Alice Wallenberg Foundation, the Wenner-Gren Foundations, the Carl Trygger Foundation and the Ministry of Education of China. This research project is part of a larger research program on photoinitiated modification of synthetic polymer to which a number of Chinese and Swedish graduate students have contributed both ideas and experimental work: Sven Gothe, Anders Hult, Jons Hilborn, Yong-li Chen, Pei-yao Zhang, Klas Allmer, Yan Qing, Bao-jun Qu, Wen-fang Shi and Zhen-gou Feng. My sincere thanks are due to all of them.

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