

Bulk Surface Photografting Process and Its Application. III. Photolamination of Polymer Films

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ABSTRACT: This paper introduces a set of new concepts related to the macromolecular design and to the practice in the realm of lamination by photografting, with experimental studies of the synthesis, structure, and performance of various systems, including valence bond adhesion of the organic polymeric materials, hyperbranched macromolecules rooted to the surface of organic substrates, macromolecular networks rooted on and bridged between two organic substrates, and a synthetic route combining primary and secondary photografting processes for the preparation of supermolecular architectures. In successful photolamination experiments based on these ideas, hyperbranched macromolecules of large size (10–20 μm) were obtained after initiation with aromatic ketones, which undergo a photoreduction reaction. A range of different organic polymeric films have been laminated. T-peel tests show most of the laminates broke inside the substrates and not at the interface between adhesive and substrate. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1723–1732, 1997

Key words: photografting polymerization; photolamination; supermolecular architecture; valence bond adhesion and photocuring

INTRODUCTION

Properties such as printability, heat sealability, and selective impermeability to oxygen and/or moisture promote the use of laminated or multilayer films to replace traditional packaging materials, such as paper, metal, and glass. The present production of laminated film is dominated by three technologies: multistep coating, lamination by solvent-borne adhesives and multilayer coextrusion.¹

Photolamination is an application of photocuring technology to adhesion which has developed

during the last decade. Since this technique meets the demands of no environmental pollution and low energy, it is developing very rapidly. Extensive research work concerning composition, formulation, and technology has been carried out,^{2,3} and some new and special applications are being exploited.^{4,5} A commercial photolaminating line for packaging production has been initiated in Germany.⁶ In principle, these technologies involve the replacement of traditional adhesives with photocuring adhesives.

The main difficulty in the lamination of polymer films or in the lamination of a polymer film to an inorganic material lies in the low surface energy of the polyolefinic materials that constitute the main polymer family (see Table I). The current methods for overcoming this problem fall into two categories. One method is to adjust the composition or recipe of adhesives to balance the adhesion forces to two different substrates. Many proprietary laminating adhesives (including adhesives used in coextrusion and irradiation curing

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Table I Surface Free Energies of Some Organic and Inorganic Materials

| Materials | Surface Free Energy (MJ/m ²) |
|--------------------------------|--|
| Polymers | |
| Teflon [®] | 19.1 |
| SBR | 29.1 |
| PE | 32.4 |
| PMMA | 40.2 |
| PS | 40.6 |
| Nylon-6,6 | 41.4 |
| PVC | 41.5 |
| PET | 45.1 |
| Inorganic Materials | |
| Mica | 120 |
| Silica | 287 |
| Al ₂ O ₃ | 577–690 |
| Silver | 890 |
| Graphite | 1250 |
| Fe ₂ O ₃ | 1357 |
| Copper | 1360 |

technology) belong to this category.^{2,7} The other method is to increase the surface energy of the polymer substrate by introducing polar functional groups onto the polymer surface,⁸ where the main methods are reactive gas discharge treatment (corona, plasma); chemical reaction (usually oxidation), which is widely used in industry; and the grafting of polar monomers onto the polymer surface.

Since 1983, Rånby et al.^{9–12} have conducted research into three aspects of polymer photochemistry, as follows.

Surface Photografting of Polymer Films and Fibers

Two different photografting systems have been invented: a vapor phase transfer batch process for films and sheets of polyolefins and polyesters; and a continuous process with presoaking for strips of polymer films, monofilaments, and textile yarns.⁹ The grafting reaction takes place in a very thin layer of solution on the film or fiber surface and gives high grafting efficiency (70 to 80%) in a rapid process (a few seconds).

Photocross-linking of high density polyethylene, (HDPE), low density polyethylene, (LDPE), and ethylene propylene diene copolymer, (EPDM) Elastomers

The photocross-linking reaction time has been shortened, the cross-linking efficiency has been

increased, and a new continuous process and industrial technique for photocross-linking PE in the melt has been developed and successfully applied in the manufacture of crosslinked polyethylene, (XLPE) insulated wires and cables for the first time.^{10,11}

Photocuring of Modified Polyesters without Styrene

Linear unsaturated polyesters and newly invented dendritic polyesters with acrylate end groups have been synthesized and photocross-linked with or without multifunctional acrylate monomers as diluent.¹²

As methods of macromolecular synthesis, these three approaches represent three different polymer reaction methods: nonhomogeneous surface grafting onto a polymer substrate; crosslinking of bulk polymer materials; and curing polymerization of polymer, oligomer, and monomer solutions.

The bulk surface photografting is a new process. The initiation, mechanism, and kinetics have been investigated in detail in two previous reports.^{13,14} This paper introduces the first application of the new process—the photolamination of two organic polymer films. This lamination is different from the traditional photolamination technology, which laminates two substrates by means of photocurable adhesives. It involves both a surface photografting polymerization onto the substrates and a curing process of the interlayer. The research work will focus on two aspects: the molecular design of the laminate structure; and the main experimental results obtained by applying the new idea, based on previous reports.^{13–15}

STRATEGY BY SURFACE PHOTOGRAFTING

Lamination Design—Chemical Bonding Adhesion

The classical adhesion principle is shown in Figure 1.

In Figure 1, S_A and S_B are the substrates to be laminated; A , B , and E are the cohesive strengths of S_A , S_B , and the adhesive, respectively; C and D are the interfacial attractive forces. The final adhesion strength of the laminate is dependent on C , D , and E .

The magnitude of E depends on the chemical composition and the final macromolecular structure in the adhesive layer, while the magnitudes

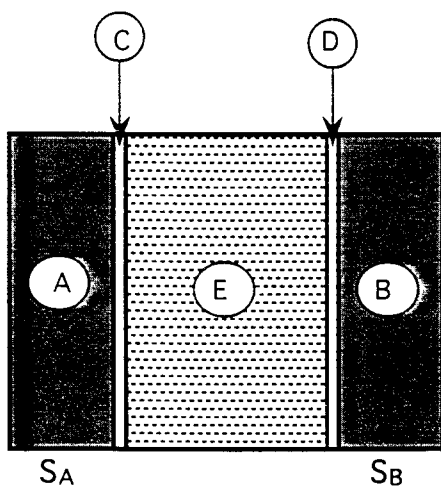


Figure 1 Schematic graph of the classical adhesion principle.

of C and D depend on the interfacial interaction and on the physical states of the substrate surfaces. The main interaction forces of adhesion and the corresponding interaction energies are listed in Table II.

Most organic polymeric materials, especially the polyolefins in which dispersion (London) forces predominate in interfacial interactions, have very low surface free energy. This low surface free energy or interaction force is the main reason why it is difficult to laminate non-polar polyolefinic substrates both with and without adhesive.

To introduce polar groups that bind chemically onto the surface of a substrate, some type of surface treatment or grafting polymerization is necessary, and these modifications create a new surface or interface. The new surface with polar

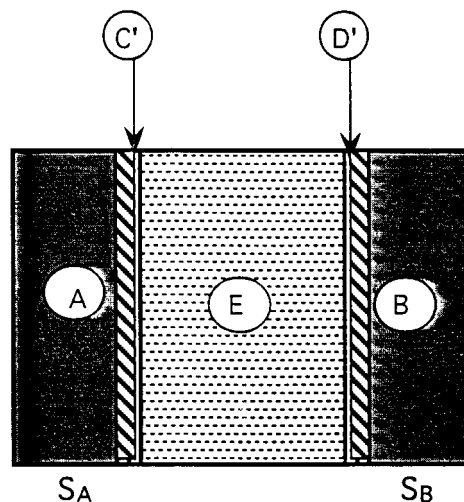


Figure 2 Schematic graph of the adhesion principle with modified surfaces of the two substrates.

groups (Fig. 2) introduces hydrogen bonds or polar forces into the interfacial interaction.

The new situation is illustrated in Figure 2 where, in relation to Figure 1, $C' > C$, and $D' > D$. Conventional technologies employed in the industrial production of laminates are based on this principle.

The question is whether it is possible to increase the interfacial interaction even further, e.g., by replacing polar and hydrogen bond forces with covalent bonds, as in Figure 3. This would make the adhesion forces comparable in strength with the cohesive strengths of the substrates and the adhesive. This is the most ideal adhesion state; chemical bond or valence adhesion, and the final laminate strength would be determined by E , A , or B .

Table II Types of Physical Attractive Forces and Interaction Energies

| Type of Force | Energy (KJ/mol) |
|------------------------|-----------------|
| Primary Bonds | |
| Ionic | 600–1100 |
| Covalent | 60–700 |
| Secondary Bonds | |
| Hydrogen bonds | 10–40 |
| Polar | 4–20 |
| Dispersion | 0,08–40 |

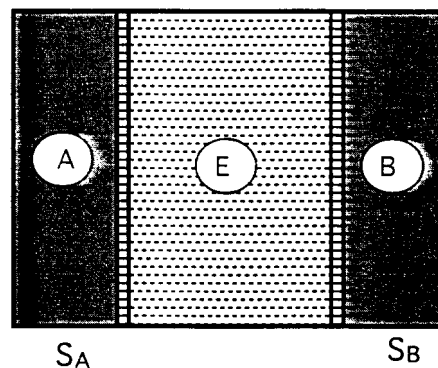


Figure 3 Schematic graph of the noninterface adhesion principle.

Priority of Surface Photografting Polymerization

To achieve the chemically bonding laminate shown in Figure 3, the key problem is to achieve chemical bonds between the substrate and the cured adhesive. With presently known techniques of macromolecular synthesis, a variety of synthetic routes can be considered. The photografting method deserves to be given priority due to the following advantages.

- 1) Photografting polymerization is based on the abstraction of hydrogen from H-donors by aromatic ketones. Most polymers, especially those with low surface free energy, contain many abstractable hydrogen atoms on their backbones or at the material surfaces. This creates a potential to laminate a large range of polymer substrates by photoinitiated grafting.
- 2) Photografting polymerization is a process in which the irradiation, initiation, and polymerization can take place simultaneously under ultraviolet (UV) radiation. It is, therefore, a convenient, easily controlled, and low cost process.

Lamination Mechanism

From the basic principles and the performance of photografting polymerization, two macromolecular bonding designs can be drawn, as shown in Figure 4.

This figure presents ideal models of the schematic structure of grafted polymer chains, terminated by adding a small radical [Fig. 4(a)] and by the coupling of two chain-end radicals [Fig. 4(b)].

Because of the practical difficulties in the lamination process, such as those due to the roughness of the substrate surface and the method application of the adhesive, the laminating layer should

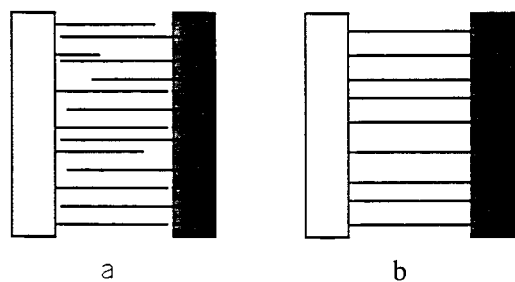


Figure 4 Ideal laminate models.

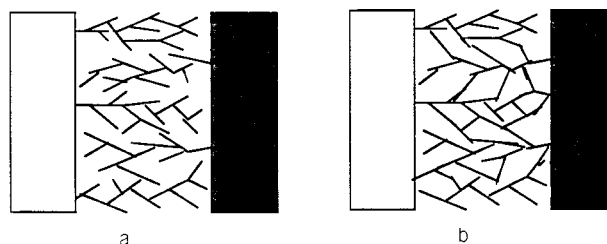


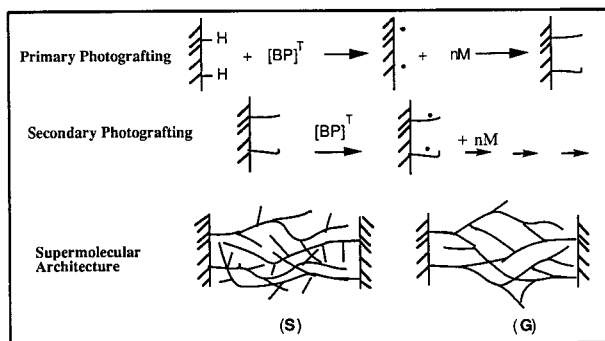
Figure 5 Laminate models based on supermolecular architectures.

be a few micrometers (μm) thick. In commercial multilayer films, the adhesive layers are 2–10 μm thick.

For the molecular bonding of two substrate surfaces, the polymer chains should be grafted to the substrates at both ends. An average distance of 6 μm between the substrate surfaces requires a molecular mass of about 2×10^6 for straight linear chains to connect the two substrates. The photografted chains are branched¹³ due to secondary grafting, and they have a coiled conformation. This means that a much higher molecular mass, e.g., 10^{10} based on a square relationship of molecular mass and gyration radius, is required for macromolecules to connect the two substrates. It is obvious that it is not possible to achieve the two structures shown in Figure 4. Therefore, two alternative new structures are proposed, as shown in Figure 5.

Figure 5(a) shows a branched tree structure rooted onto the polymer substrates, and Figure 5(b) represents a cured (cross-linked) network structure rooted onto the two different polymer substrates, which become linked by the macromolecular network.

In comparison with Figure 4, the new feature of Figure 5 is the branching of the macromolecular chains. In a previous publication,¹⁵ we have presented the concepts of primary and secondary photografting polymerizations. The primary photografting results in the formation of a simple monochain macromolecular structure, as shown in Figure 4(a), while secondary photografting results in the formation of a grafted branched polymer (Scheme 1). The polymerization develops in a successive pattern as follows where *S* and *G* represent, respectively, a hyperbranched graft macromolecule and a crosslinked macromolecular network obtained by adding multifunctional monomers. Obviously, the propagating model makes it possible that the grafted branched polymer can reach the scale of the laminate dimen-



Scheme 1 Primary photografting, secondary photografting, and supermolecular architecture in lamination by photografting.

sions in size. The combination of primary and secondary photograftings can give the supermolecular architectures of Figure 5 by UV irradiation.

With present analytical methods, it is not easy to characterize the two kinds of supermolecular structures (*S* and *G*) because the adhesive molecules are connected chemically to the surfaces of the substrate. The molecular mass and distribution of the branch chains, the number of grafted chemical bonds, and the gross molecular mass and the degree of branching of the supermolecular architecture cannot be directly measured; but it is possible to prove the existence of this kind of supermolecular structure by indirect methods. For example, the solvent separability and nonseparability of the laminates in suitable solvents can be used to confirm the existence of a branched or crosslinked network structure; the thickness of the laminating layer and the grafting efficiency can be used to estimate the dimensions of the supermolecular architecture.

EXPERIMENTAL

The photografting laminations of polymeric films were conducted in a UV curing reactor, which was operated in the same way as in the previous reports.¹⁵

Benzophenone (BP), 4,4'-dichloro-benzophenone (DCBP), benzoyldimethylketal (BDK), and hydroxycyclohexyl acetophenone (Irgacure 184) were used as photoinitiators. The monomers used were mainly acrylate compounds: AA refers to acrylic acid, BA to butyl acrylate, and QB to hydroxyethyl acrylate in this work. The films used in photolamination (LDPE, HDPE, PP, OPP, PET, and Nylon 66) are commercial products.

Adhesion measurements were carried out as 180 degree peel test (T-peel test) using an Instron 1122 with an extension speed of 20 mm/min. The width of test strips was 19 mm. To prevent extension of the flexible substrates, Scotch tape was applied on both sides of the laminate.

PRINCIPAL VARIABLES INVOLVED IN THE PHOTOLAMINATION PROCESS

Since the formation of the cross-linked network structure [Fig. 5(b)] is not sensitive to the laminating conditions, the quantitative and qualitative experiments must be performed mainly on the model of Figure 5(a). Considering the difference in polarity of the polymer substrates, LDPE||LDPE has been used as a representative of the nonpolar//nonpolar film laminates, and LDPE||PET has been used as a representative of nonpolar//polar film laminates.

Evolution of Lamination

Since the photolaminating or photocuring reaction between the two substrates begins at the two substrate surfaces, i.e., the chemical bonds connecting the substrate and the photosetting adhesive are formed first, the cohesive strength of the cured adhesive will be the decisive factor for the laminate strength. In the course of the photopolymerization, two physical variables determine the magnitude of this cohesive strength. One is the size of the branched molecules which propagate during UV irradiation; another is the change from

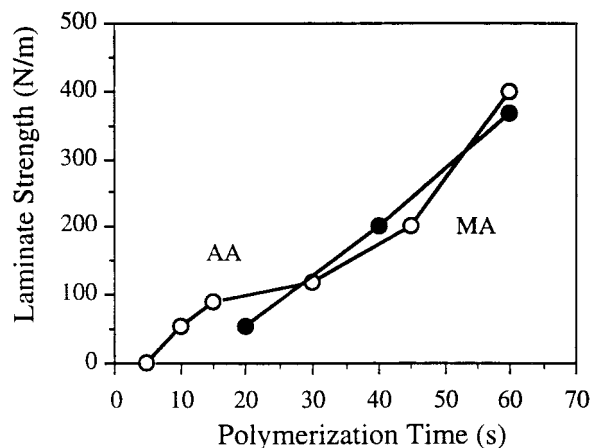
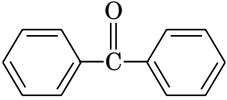
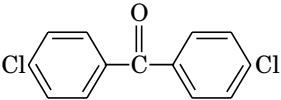
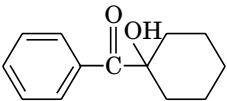
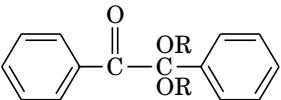


Figure 6 Relationship of T-peel strength versus photolaminating time (50°C; 2 wt % BP).

Table III Performance of Photoinitiators in Photolamination^a

| PI | Molecular Formula | Laminate Strength (N/m) | |
|-------------|---|-------------------------|-----------|
| | | LDPE LDPE | LDPE PET |
| BP |  | 90 | 110 |
| DCBP |  | 158 | 95 |
| Irgacure184 |  | 0 | 5.2 |
| BDK |  | 0 | 6.3 |

^a 50°C; AA; 2 wt %; photoinitiator. R is CH₃.

liquid to solid state as the polymerization develops. The strength of the laminate increases with increasing polymerization time, as shown in Figure 6. These results show that a necessary condition to obtain a good bonding is that the rate of polymerization conversion is high.

Photoinitiators and Concentration

As expected, two different commercial photoinitiators (PI) show different performance in photolamination (Table III). BP and its derivatives, which react mainly by hydrogen abstraction from the surface of the substrate, are efficient in photolamination applications. Irgacure 184 and BDK, which mainly undergo cleavage reaction to two radicals, merely result in the formation of homopolymer and cannot, therefore, give any significant contribution to lamination by photografting.

The effect of photoinitiator concentration on the lamination process is shown in Figure 7. For LDPE||LDPE lamination, the strength of the bond between the two substrates increases at low concentrations of photoinitiator and decreases at concentrations over 5 wt %. This observation may be accounted for by assuming that the increase in BP concentration leads to two opposite effects simultaneously: the number of chemical bonds per unit area of the surface increases, which is posi-

tive for lamination; while the average length of the whole molecule and its branched chains decreases, which is negative for lamination strength. These two opposite effects result in a maximum as shown in Figure 7.

In the LDPE||PET system, a different result was obtained. In this case, the strength decreased with increasing BP concentration without any maximum. This behavior can be accounted for because the PET film has a highly active surface for hydrogen abstraction.¹⁴ The maximum number of

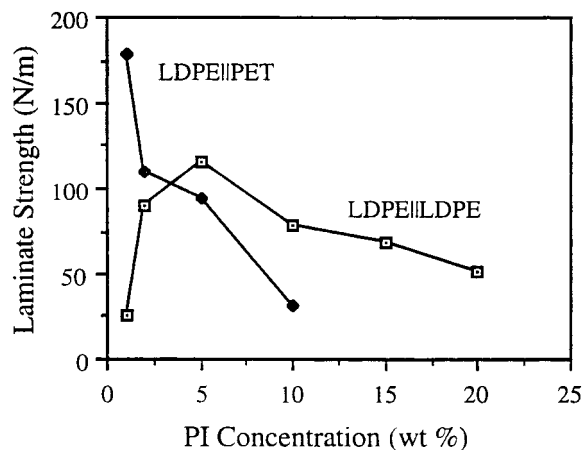


Figure 7 Effect of photoinitiator concentration on T-peel strength of laminates (50°C; AA).

initiated sites is reached at a very low PI concentration, and the effect of decreasing chain length dominates throughout the experimental range.

Monomers

The monomer is the main component of the photolaminating adhesive layer. For the selection and evaluation of the monomer, three aspects have to be considered.

Photopolymerization Reactivity

In the photolamination process, irradiation and polymerization are almost simultaneous. The photopolymerization reactivity of the monomer determines directly the on-line lamination rate. Hence, it is important that the monomer has a high photopolymerization reactivity. The extensive experimental results in our work have shown that acrylate monomers have the highest photopolymerization reactivity among monomers that undergo free radical chain polymerization.

Photografting Reactivity

The photografting reactivity of a monomer includes two aspects: the first is the photopolymerization reactivity; the second is the extent to which monomers meet the following requirements with regard to chemical structure.

- 1) The monomers should have no active hydrogens on their structure because they could act as centers to initiate homopolymerization.
- 2) There should be active hydrogens on the backbone of the grafted polymer formed so that a secondary photografting process can easily be initiated from these points.

The experimental results are in accordance with these requirements, and acrylic acid and acrylonitrile are the best monomers for this application; while methacrylate monomers show an inferior performance due to their content of allylic hydrogen atoms.

Wetting Match

In laminating formulations, monomers actually fulfill two functions. As the main polymerization component, the monomer should produce a cured film with a certain cohesive strength. The monomer and substrate should therefore have slightly

different surface tensions in order to avoid the monomer being absorbed by the substrate. In systems such as LDPE||BA, PC||AA, and NYLON||AA, such an absorption effect can be observed. On the other hand, monomers also serve as a solvent or carrier to transport the photoinitiator to the substrate surface. If a monomer cannot spread fairly evenly on the substrate surface, the surface hydrogen abstracting reaction will obviously be influenced. In some cases, such as LDPE||QB and OPP||AA, a negative effect can be observed. The monomer should therefore have quite good ability to wet the surface of the substrate. This contradiction means that the monomer composition and the substrate surface should have a wetting match. This wetting match can be adjusted by additives or comonomers.

Temperature

The effect of temperature on the photolaminating process is shown in Figure 8. The tendency shown in Figure 8 is similar to that of increasing photoinitiator concentration on the laminating process. One effect of increasing temperature is that the number of the surface-grafted sites increases, which is beneficial for adhesion. When the branch chains become shorter, the adhesion will eventually deteriorate.

The optimum temperature value is dependent on the surface activity of the substrates. It is lower for LDPE||PET than for the inert LDPE||LDPE assembly.

Thickness of the Photolaminated Adhesive Layer

According to the general adhesion theory, the thickness of the adhesive layer can have either a

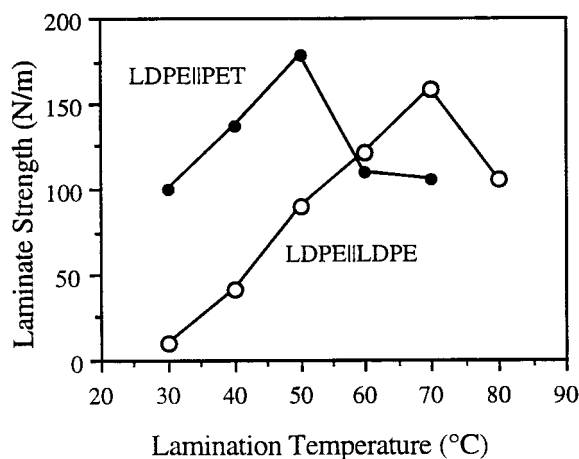


Figure 8 Effect of the laminating temperature on T-peel strength (AA; 1 wt % BP).

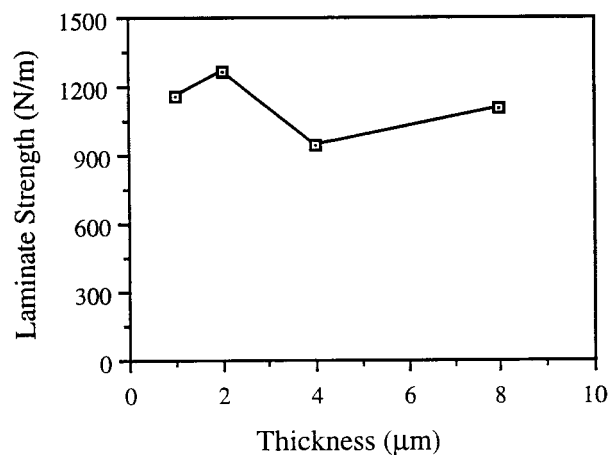


Figure 9 Effect of the thickness of the lamination adhesive on T-peel strength (AA; 5 wt % BP; 50°C).

negative or a positive effect in different systems. For flexible polymer substrates, an increasing thickness up to a few mm has positive effect. For the present lamination system, with its character of thin substrates and thin adhesive layers, the effect is slightly negative (Fig. 9). Therefore, it is meaningful to reduce the thickness of the lamination layer as much as possible because a thin adhesive layer responds to shorter photolamination times than a thicker layer.

NOVELTIES AND APPLICATIONS

New Supermolecular Architecture

The structure of synthetic polymers have become more and more complicated. Historically, polymer structures have developed as follows: linear molecules, branched molecules, block molecules, star-shaped molecules, comb-shaped molecules, grafted molecules, cyclo-shaped molecules, rotaxane, and dendrimers (including telechelic oligomers). Compared with these molecules of different shapes, the design of the molecules shown in Figure 5 can be characterized as follows:

- 1) branched and cross-linked macromolecules of very large molecular size and complicated molecular structure;
- 2) macromolecules grafted onto polymer substrates;
- 3) macromolecules with details of the structure controlled by composition and technology.

These three characteristics are the main reason why we claim that the design of the structure in Figure 5 represents a new supermolecular architecture.

New Polymer Forming Method

Traditional photolamination is a non-solvent photocuring system or bulk forming system, where bonding of the substrates is achieved by the adhesion forces between the cured adhesive and the two substrate surfaces.

The earlier photografting polymerization is conducted in a vapor phase or a solution phase. The two photografting processes, both involved in a multistep operation with coating (precoating), irradiation, and post-treatment, produced the surface-grafted polymer. These processes result in a modification of the polymer surface. The present photografting lamination technique is a combination of the two processes: surface grafting and bulk photolamination. Lamination by photografting produces a new supermolecular architecture and it is, therefore, a new polymer-forming method.

New Applications

Under the premiss that one of the two substrates is transparent to UV radiation, especially in the far UV (200–300 nm), most organic polymer films can be combined. Table IV lists some practical examples.

The laminates presented in Table IV have a combination of special properties, such as sealability, printability, permeability, and machining and mechanical properties. They bring films with different characters together, giving multilayer films for particular and new applications; e.g., lamination of polyvinylidene chloride (PVDC) and LDPE gives an inexpensive high barrier bilayer packaging film of high strength, and the lamination of LDPE and PET or LDPE and Nylon 66 produces composite films with balanced barrier properties for O₂ and water vapor, and are easily heat-sealed and printed. The main advantage of the photografting lamination technique over the multilayer extrusion process is that photografting can greatly enlarge the family of laminates without limitations in thermoplastic, surface tension, and rheological properties. In contrast to the photocuring laminating process, the photografting technique has the following characteristics: the interface between the substrate and the cured ad-

Table IV Different Types of Photografted Laminates and Laminates Strength

| Laminate (thickness, mm) | Laminating Time (s) | Failure Side (Broke) | T-Peel Strength (Broke, N/m) |
|-------------------------------------|------------------------|-------------------------|---------------------------------|
| LDPE LDPE (0.188 0.188) | 25 | LDPE | 1050 |
| LDPE LDPE (0.083 0.083) | 15 | LDPE | 520 |
| PP PP (0.1 0.1) | 45 | PP | 2310 |
| HDPE HDPE (0.04 0.04) | 100 | HDPE | 290 |
| LDPE PET (0.188 0.256) | 15 | LDPE | 1050 |
| HDPE PET (0.04 0.256) | 30 | HDPE | 530 |
| PP PET (0.1 0.256) | 20 | PP | 1580 |
| OPP PET (0.018 0.256) | 50 | OPP | 630 |
| LDPE NYLON-66 (0.188 0.12) | 10 | LDPE | 1340 |

hesive is molecularly bonded; the crosslinked network structure formed by adding a multifunctional monomer to the adhesive layer makes the laminate resistant to delamination by heat and solvents; and laminates with a superbranched molecular structure will be solvent-separable and reversible.

Since the photografting lamination technique depends not on secondary molecular forces between adhesive and substrate but on chemical bonding, it can be applied to any substances containing no groups that have any negative effect on the process of photografting. Special properties can be achieved by mixing some special components into the photopolymerizable layer. This means that the laminate can be functionalized by deliberate choice of the composition of the photolaminating layer. An example is that an adhesive recipe with AA as main component gives bilayer laminate barrier properties toward O₂, which are comparable with those of pure PVDC and can be obtained with OPP film as substrate.

CONCLUSIONS

A new photografting lamination technique has been developed based on the primary and the secondary photografting polymerization between two film substrates. This results in the formation of

two new supermolecular architectures: superbranched macromolecules and macromolecular networks, both grafted onto the surface of the polymer substrates. These new supermolecular architectures form a new type of adhesion and lamination where the interface has covalent bonds to the substrates.

Photolamination experiments based on these ideas have proved to be successful. With aromatic ketones, which undergo photoreduction by hydrogen abstraction and acrylic monomer compositions, a large range of organic polymeric films have been laminated to composite membranes with a high delamination peel strength and high barrier properties to, e.g., oxygen and water vapor.

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