

Surface Modification by Continuous Graft Copolymerization. II. Photoinitiated Graft Copolymerization onto Polypropylene Film Surface

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SYNOPSIS

A method for photochemically induced graft copolymerization of acrylamide (AM) onto polypropylene (PP) film surface by a continuous presoaking process under nitrogen atmosphere has been developed. After removal of homopolymer formed, ESCA, UV spectroscopy, contact angle, and adhesion measurements confirmed a photografted layer on the surface of the PP film. The results from spectral analysis and surface properties measurements were consistent. The best grafting yield was obtained for 7–10 s irradiation time. Stabilizing additives in the PP film had no evident effect on the photografting. Benzophenone was an efficient photoinitiator for photografting of PP film with AM. An AM concentration of 0.5–1.3 *M* in the presoaking solution was appropriate in the present case. Acetone was the best solvent among the three alifatic ketones tested (acetone, methylethylketone, and methylpropylketone).

INTRODUCTION

Polypropylene (PP) is a polymer of fast growing commercial importance. However, this polymer has some drawbacks: It does not contain reactive sites, it has extremely low hygroscopicity, and it is difficult to dye and laminate, due to its low adhesion. To modify these properties of PP, photochemical grafting methods have attracted considerable interest for about 20 years.^{1–14} Surface properties are as important as bulk properties when PP is used as film, plate, or fibre. In some published work, high grafting yields are reported, and in these cases the bulk properties of the base polymer are altered by the grafting. Tazuke et al.^{8,13,15} reported photografting onto PP film surface and studied the influence on the grafting of initiator and additives and changes in the extension of hard elastic PP film when stretched. However, no study has been reported so far on any continuous process for grafting using short irradiation times.

In our previous papers,^{16–18} acrylamide (AM) and acrylic acid (AA) were photografted successfully onto polyethylene tape film, PET, and PP fibre using the presoaking process we developed with the purpose of practical applications. This article deals with photografting of AM onto PP film surface using the same process. The reaction was primarily at the surface of the PP film and led to modifications of the surface (increased hydrophilicity, adhesion, dyeability, etc.) of the photografted film material.

EXPERIMENTAL

Materials

The PP film, supplied by Oy W. Rosenlew AB., Finland, was of three kinds:

1. PP blown film without additives, 220 μm thick,
2. PP blown film with stabilizing additives, 220 μm thick, and
3. PP tape film (stretched) with stabilizing additives, 60 μm thick.

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The additives in PP blown film and tape film consisted of about 2% CaCO₃, 0.2% Tinuvin 770, 0.1% Chimassorb 944, and 2% LDPE (added as masterbatch).

Acrylamide (AM), CH₂=CHCONH₂, Merck, synthetic grade, 99% (GC), was recrystallized from acetone before use. Benzophenone (BP), C₆H₅COC₆H₅, Merck, synthetic grade, 98% (GC), was used without purification. Acetone, CH₃COCH₃, Merck, analytical grade, min. 99.5%, methylethylketone (MEK = butanone). CH₃COCH₂CH₃, Kebo puriss, Halt min. 99%, and methylpropylketone (MPK = pentanone-2), CH₃COCH₂CH₂CH₃, Merck, synthetic grade, 98% (GC) were used without purification. A crystal violet indicator, C₂₅H₃₀N₃Cl, Merck, was used for microscopy (*M* = 407.99 g/mol). Araldite D, CIBA-GEIGY, a clear, pale yellow liquid resin with epoxy content 4.1–4.5 mol equiv/kg, was used. The curing agent was HY956, CIBA-GEIGY, a clear, pale yellow liquid. The UV light source was PHILIPS HPM-15, a high-pressure metal halide lamp with lead and gallium iodide additives. It was made of ozone-free quartz with an active radiation between 320–440 nm.

Photografting Polymerization Procedure

The device used here was the same as described before.¹⁶ The PP film was passed through the presoaking vessel and then through the reaction chamber at different speeds, which gave irradiation times of the film varied from about 4–200 sec. Different AM and BP concentrations in the presoaking solution and three different ketones as solvent have been investigated. Five mm film strips were used.

The reaction chamber was closed and filled with a flow of nitrogen gas during the reaction period. The exhaust gas containing nitrogen and vapour of solvent, monomer, and initiator escaped through the outlet. The reaction temperature measured by a shielded thermocouple in the reaction chamber was 68–74°C. Acrylamide vapour sublimated from solid acrylamide in a vessel under the running roll. The vapour pressure of AM was 0.029 mmHg at 40°C and 2 mmHg at 87°C. The distance from the UV light source to the film surface was 20 cm. The film passed through the presoaking solution for a time period that was about one third of the irradiation time. The time for the film from leaving the presoaking solution to entering the reaction chamber was about two fifths of the irradiation time of the film.

After the photografting process, the film was immersed in acetone for 30 min, and washed thor-

oughly to remove monomer and initiator from the film surface. The film was then immersed in hot water (85–92°C) for 30 min, and washed thoroughly to remove AM homopolymer from the film surface. The film was finally rinsed with water and dried at room temperature.

Analysis

For polymer surface analysis, ESCA is a very useful and powerful method. In our case, the relative intensity of the ESCA lines for N_{1s} over C_{1s} was used to indicate the grafting yield. The ESCA analysis was performed by using a Leybold Heraeus ESCA/Auger Spectrometer LH 2000 unit with computer online.

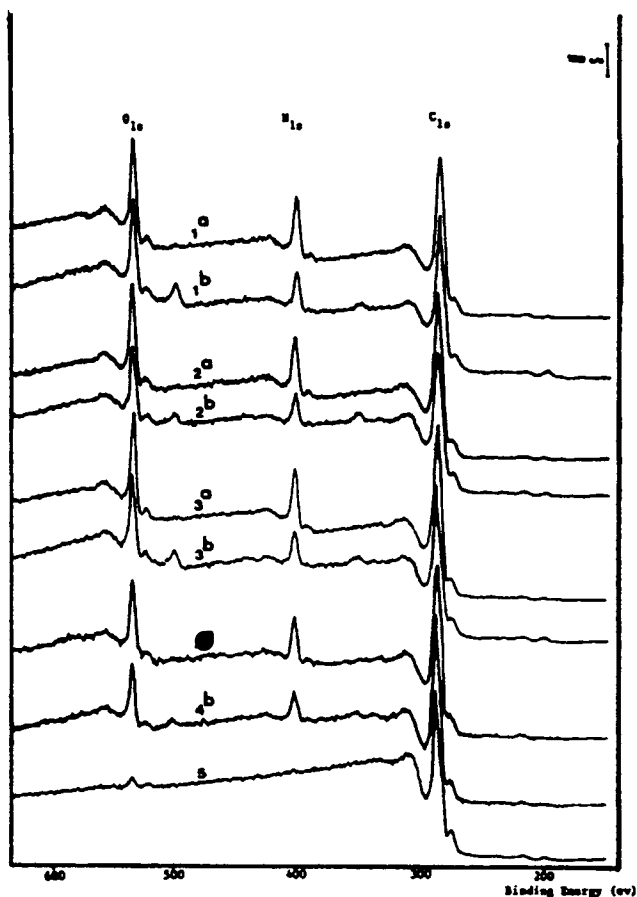


Figure 1 ESCA spectra of photografted PP blown film without additive. Irradiation time: 10 sec in 1, 2, 3, 4, and 0 sec in 5; presoaking solution: [BP] = 0.2M, [AM] = 1.3, 0.8, 0.5, 0.2M in 1, 2, 3, 4, acetone as solvent. a, grafted copolymer + homopolymer; b, grafted copolymer (homopolymer removed by extraction). The weak ESCA lines at 500 and 350 ev are probably due to impurities of metal ions in the distilled water for washing (Na⁺, Ca²⁺).

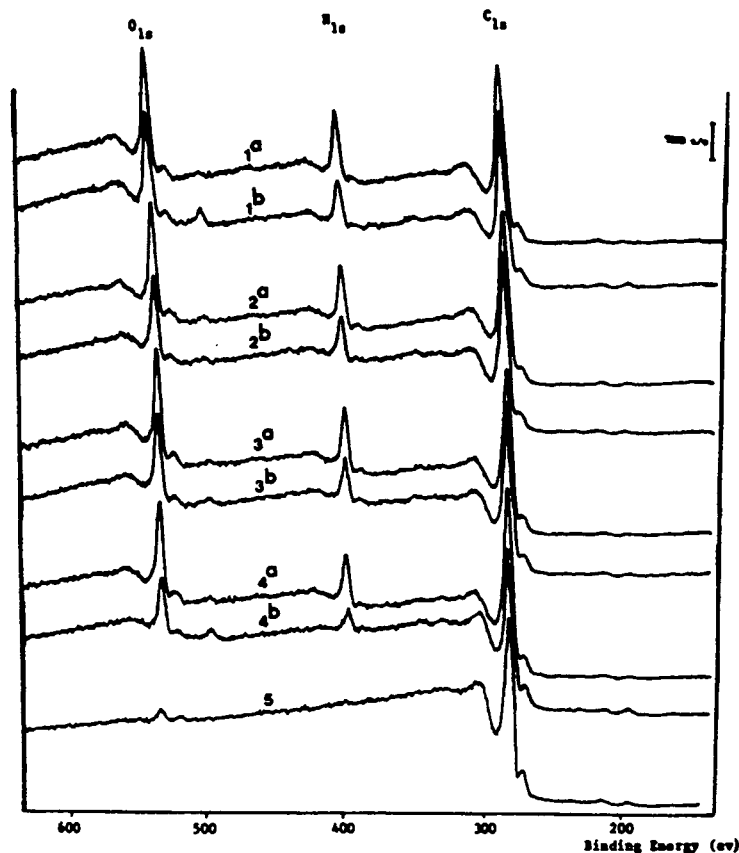


Figure 2 ESCA spectra of photografted PP blown film with additive. Irradiation time: 10 sec in 1, 2, 3, 4, and 0 sec in 5; presoaking solution: [BP] = 0.2M, [AM] = 1.3, 0.8, 0.5, 0.2M in 1, 2, 3, 4, acetone as solvent. a, grafted copolymer + homopolymer; b, grafted copolymer (homopolymer removed by extraction).

To characterize surface properties, we measured contact angle with double-distilled water, adsorption of dye, and adhesion to epoxy resin. The contact angle of two drops of double-distilled water on the surface of the PP film was determined by using a goniometer from Rame Hart Inc. (Model A-100).

A Perkin-Elmer UV spectrometer (Model Coleman 575) was used for measurement of the dye adsorbed on the PP blown film surface. An Instron (Model 1122) Universal Testing Instrument was used for measurement of adhesion of PP tape film to Araldite epoxy resin.

RESULTS AND DISCUSSION

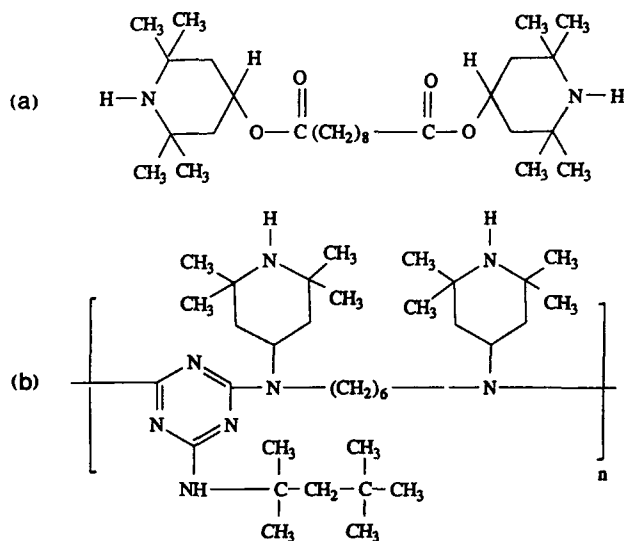
Effect of Various Kinds of PP Film

The mechanism of photografting of AM onto PP film surface was assumed to be the same as for polyethylene, i.e., the graft copolymerization was initiated by abstraction of hydrogen from the PP film

surface, caused by the triplet excited state of BP molecules. The graft yield was so small that the weight increase of the grafted film could not be detected gravimetrically. However, the N_{1s} signal in ESCA spectra of the grafted PP film surface clearly indicated that chemical photografting had indeed taken place and produced a distinct grafted layer on the surface of the PP film as shown in Figures 1-3.

It is appropriate to point out that no N_{1s} signal could be found in the ESCA spectrum of PP film with additive, although both Tinuvin 770 and Chimassorb 944 contain nitrogen. This indicated that no measurable diffusion of these two additives from the bulk polymer to the surface occurred.

In our experiments, with AM concentrations of 0.5-0.8M, the relative intensities of the ESCA lines for grafted PP blown film with additive are somewhat higher than those of grafted PP blown film without additive, but the difference is small. The additives have evidently no detrimental effect on the photografting of the PP film [as shown in Figs. 11 (a) and (b)]. This indicates that commercial PP



Chemical structure of (a) Tinuvin 770 and (b) Chimassorb 944 (a polymer of low molecular weight).

with stabilizing additives can be modified without pretreatment by using this process.

The resolved C_{1s} signal of ESCA spectra of grafted film indicates the appearance of $>C=O$ groups (as shown in Fig. 4) due to the grafted copolymer layer of polyacrylamide chains on the surface of the PP film.

Homopolymer of AM is also formed during the grafting process. Figures 1-3 show the differences in ESCA spectra of grafted PP film with and without homopolymer. The formation of homopolymer is related to the irradiation time, the concentration of monomer in the presoaking solution, and the type of PP film grafted. To obtain low amounts of homopolymer, it is favourable to use short irradiation time, 7-10 sec, high AM concentrations, and blown PP film.

Compared with blown film, PP tape film is less reactive in grafting (as shown in Fig. 7). It seemed

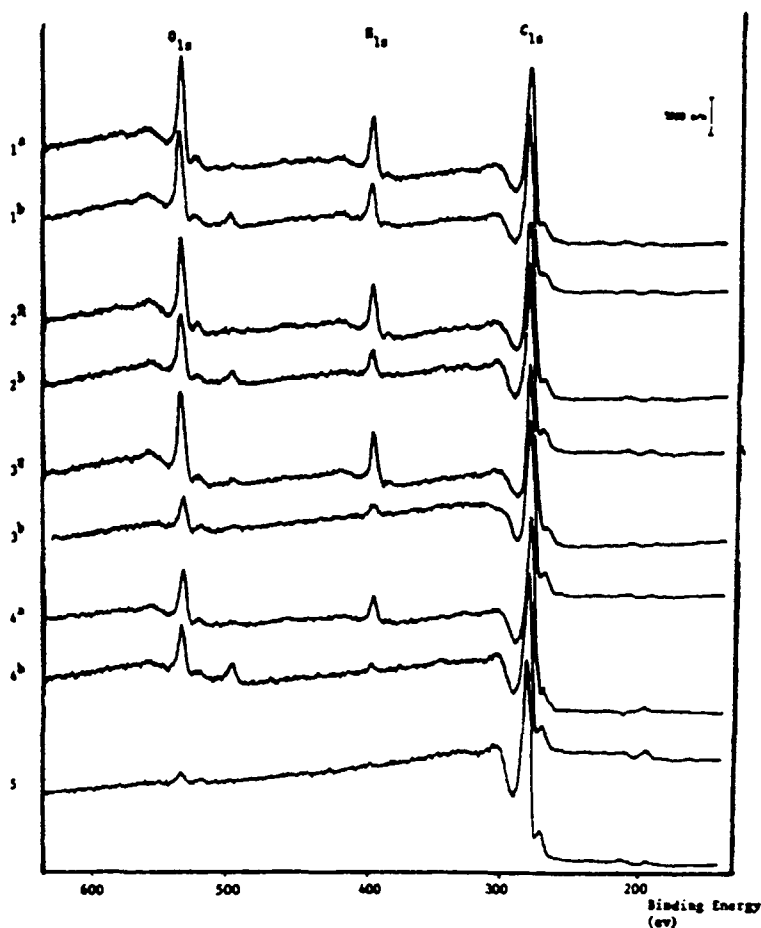


Figure 3 ESCA spectra of photografted PP tape film with additive. Irradiation time: 10 sec in 1, 2, 3, 4, and 0 sec in 5; presoaking solution: $[BP] = 0.2M$, $[AM] = 1.3, 0.8, 0.5, 0.2M$ in 1, 2, 3, 4, acetone as solvent. a, grafted copolymer + homopolymer; b, grafted copolymer (homopolymer removed by extraction).

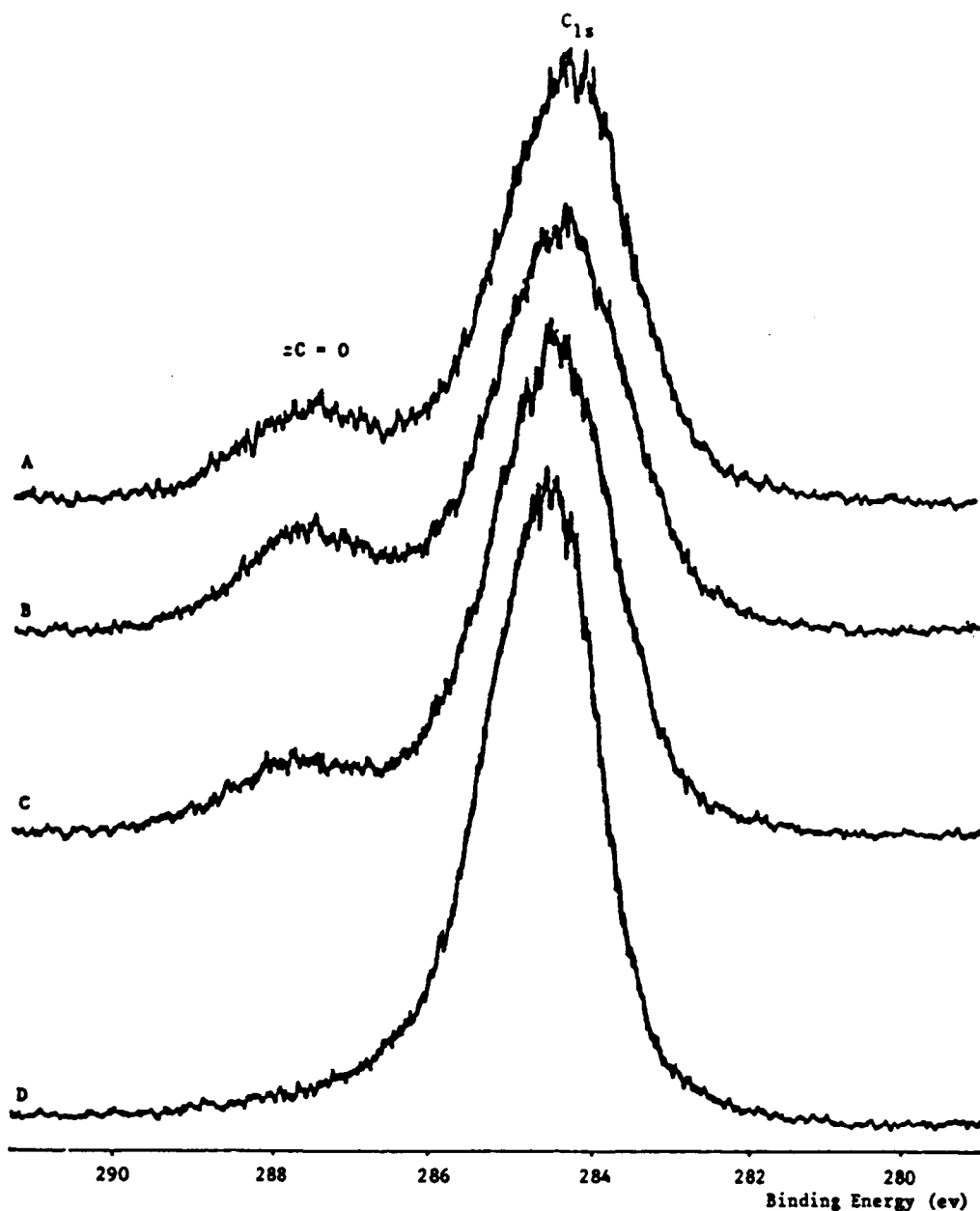


Figure 4 The C_{1s} bond in ESCA spectra of grafted PP blown film (with additives). Irradiation time: 10, 7, 4, 0 sec in A, B, C, and D; presoaking solution: $[BP] = 0.2M$, $[AM] = 0.8M$, acetone as solvent. The $=C=O$ line is due to the surface-grafted polyacrylamide.

likely that the high crystallinity of the PP tape film decreases the adsorption and penetration of presoaking solution into the base polymer surface, which may be a rate-controlling step of the grafting reaction.

Effect of Monomer Concentration in the Presoaking Solution

The AM concentration in the presoaking solution affects the photografting yields drastically as shown in Figures 5–7, which give the results from ESCA

measurements. Within a certain range of irradiation times, the higher AM concentration in the presoaking solution, the higher is the photografting yield. This may be due to increased chain length of grafted polymer with increasing $[AM]$. The difference for 0.8 and 1.3M AM is sometimes small (Fig. 6). Short irradiation time is favourable for high photografting yield both at high and low AM concentration. Similar behaviour has also been observed in the case of HDPE tape film and PET and PP fibers.^{16–18}

The results of contact angle measurement with

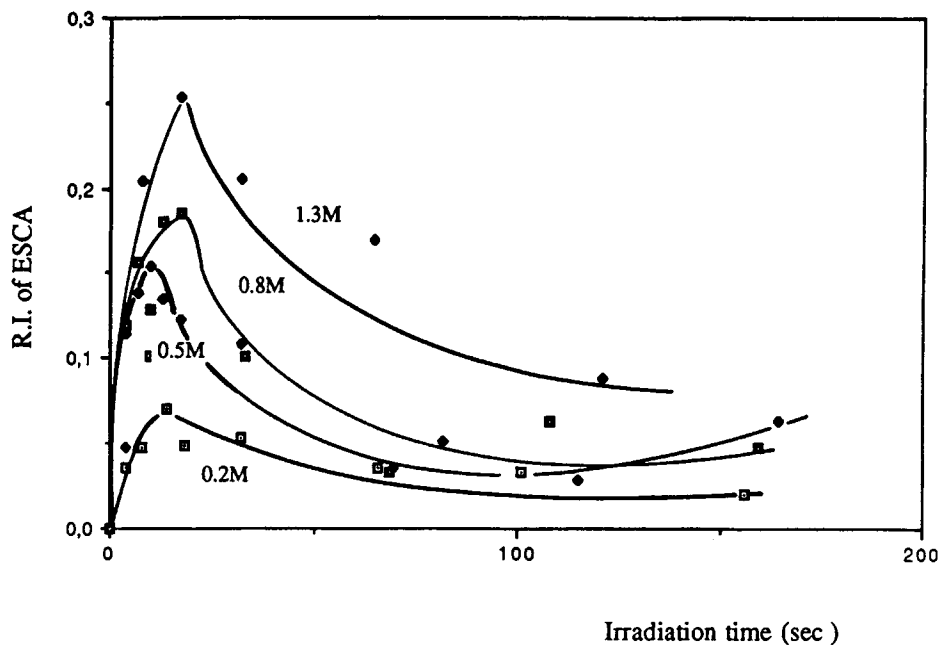


Figure 5 Effect of [AM] on photografting, PP blown film without additive. Presoaking solution: [BP] = 0.2M, acetone as solvent.

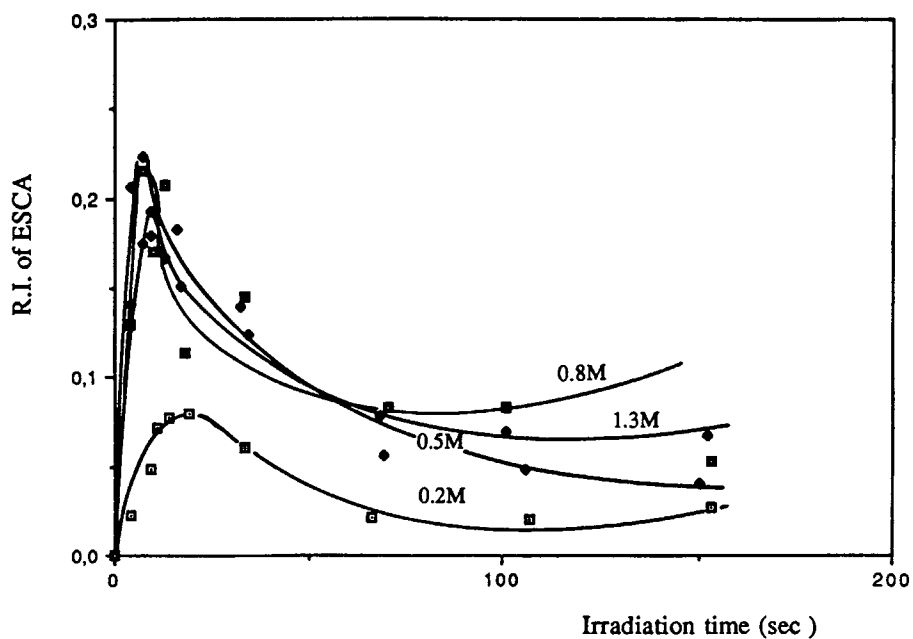


Figure 6 Effect of [AM] on photografting, PP blown film with additive. Presoaking solution: [BP] = 0.2M, acetone as solvent.

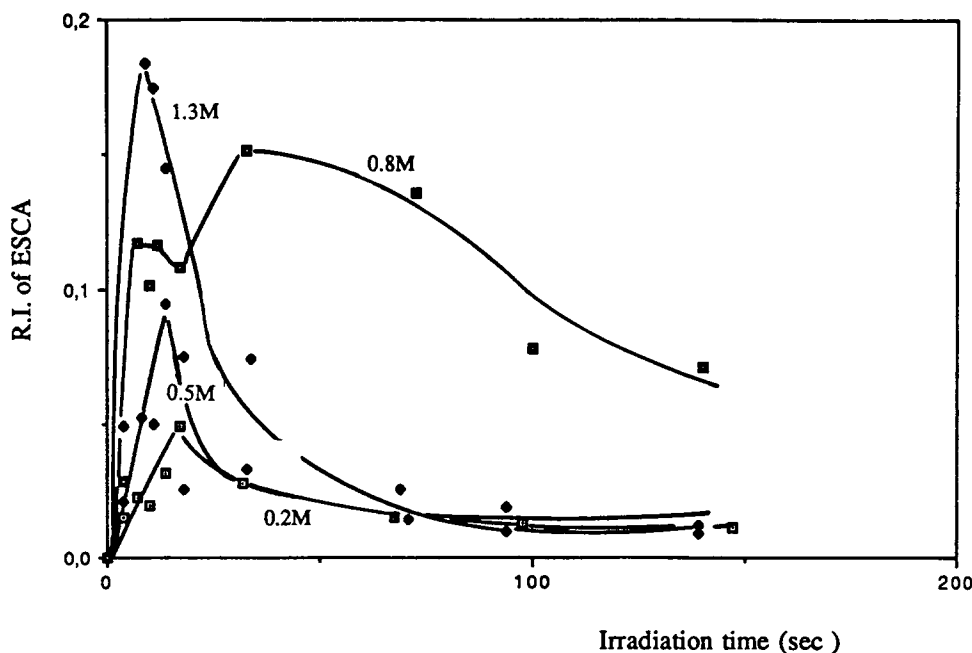


Figure 7 Effect of [AM] on photografting, PP tape film with additive. Presoaking solution: [BP] = 0.2M, acetone as solvent.

distilled water and adhesion of PP tape film to epoxy resin are consistent with the ESCA measurements as shown in Tables I–III. On the basis of the results of these experiments, a plot of contact angle of grafted PP film with distilled water versus relative intensity of N_{1s}/C_{1s} ESCA lines is given in Figure 8. For 7–10 sec irradiation time, the contact angle of PP film with distilled water is decreased from 90 to 30°.

The UV absorption spectrum of PP blown film dyed by dipping into an aqueous solution of crystal violet showed clearly the increased hydrophilicity of grafted PP film. Crystal violet has a strong UV absorption peak at 582 nm (Fig. 9). In Figure 10, the difference of dyeability of grafted PP blown film is measured at the absorption band around 582 nm of the samples. Fig. 11 shows the effect of different solvents.

Table I Contact Angle (CA) of PP Blown Film (without Additive) with Distilled Water, Grafted with Various AM Concentrations and [BP] = 0.2M in the Presoaking Solution, Acetone as Solvent

| [AM] = 0.2M | | [AM] = 0.5M | | [AM] = 0.8M | | [AM] = 1.3M | |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) |
| 0 | 91 | 0 | 91 | 0 | 91 | 0 | 91 |
| 4 | 54 | 4 | 59 | 4 | 36 | 4 | 48 |
| 8 | 55 | 7 | 41 | 7 | 35 | 8 | 31 |
| 10 | 54 | 10 | 39 | 10 | 36 | 10 | 33 |
| 14 | 60 | 13 | 40 | 13 | 33 | 14 | 25 |
| 18 | 68 | 17 | 41 | 17 | 31 | 19 | 35 |
| 32 | 75 | 32 | 51 | 33 | 50 | 32 | 34 |
| 66 | 66 | 70 | 68 | 69 | 67 | 65 | 38 |
| 101 | 64 | 115 | 76 | 108 | 61 | 82 | 64 |
| 156 | 76 | 164 | 76 | 159 | 80 | 121 | 42 |

Table II Contact Angle of PP Blown Film (with Additive) with Distilled Water, Grafted at Various AM Concentrations and [BP] = 0.2M in the Presoaking Solution, Acetone as Solvent

| [AM] = 0.2M | | [AM] = 0.5M | | [AM] = 0.8M | | [AM] = 1.3M | |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) |
| 0 | 91 | 0 | 89 | 0 | 91 | 0 | 91 |
| 4 | 71 | 4 | 29 | 4 | 33 | 4 | 46 |
| 9 | 56 | 7 | 24 | 7 | 36 | 7 | 31 |
| 11 | 53 | 9 | 26 | 10 | 30 | 9 | 27 |
| 14 | 51 | 12 | 34 | 13 | 31 | 13 | 35 |
| 19 | 48 | 16 | 32 | 18 | 38 | 17 | 31 |
| 33 | 62 | 32 | 55 | 33 | 40 | 34 | 47 |
| 66 | 66 | 69 | 44 | 70 | 55 | 68 | 54 |
| 107 | 72 | 106 | 59 | 101 | 56 | 101 | 48 |
| 153 | 78 | 150 | 67 | 153 | 64 | 152 | 49 |

Table III Contact Angle of PP Tape Film with Distilled Water and Adhesion to Araldite Epoxy Resin, after Grafting with Various AM Concentrations in the Presoaking Solution, Acetone as Solvent

| [BP] = 0.2M, [AM] = 0.2M | | | [BP] = 0.2M, [AM] = 0.5M | | | [BP] = 0.2M, [AM] = 0.8M | | | [BP] = 0.2M, [AM] = 1.3M | | |
|--------------------------|-------------|-------------------------------|--------------------------|-------------|-------------------------------|--------------------------|-------------|-------------------------------|--------------------------|-------------|-------------------------------|
| Time (s) | CA (degree) | Adhesion (N/mm ²) | Time (s) | CA (degree) | Adhesion (N/mm ²) | Time (s) | CA (degree) | Adhesion (N/mm ²) | Time (s) | CA (degree) | Adhesion (N/mm ²) |
| 0 | 91 | 0.292 | 0 | 90 | 0.282 | 0 | 91 | 0.375 | 0 | 91 | 0.425 |
| 4 | 74 | 0.479 | 4 | 72 | 0.499 | 4 | 71 | 0.625 | 4 | 58 | 0.871 |
| 7 | 70 | 0.539 | 8 | 58 | 0.887 | 7 | 47 | 1.211 | 9 | 24 | 1.711 |
| 10 | 65 | 0.503 | 11 | 53 | 0.823 | 10 | 44 | 1.186 | 11 | 23 | 1.704 |
| 14 | 58 | 0.638 | 14 | 41 | 1.197 | 12 | 40 | 1.321 | 14 | 33 | 1.727 |
| 17 | 47 | 0.818 | 18 | 61 | 0.594 | 17 | 46 | 1.243 | 18 | 50 | 1.107 |
| 32 | 63 | 0.588 | 33 | 45 | 0.899 | 33 | 44 | 1.691 | 34 | 47 | 1.101 |
| 68 | 60 | 0.469 | 69 | 68 | 0.610 | 73 | 35 | 1.592 | 71 | 67 | 0.529 |
| 98 | 70 | 0.472 | 94 | 74 | 0.601 | 100 | 44 | 1.101 | 94 | 83 | 0.458 |
| 147 | 80 | 0.454 | 139 | 81 | 0.431 | 140 | 56 | 1.040 | 139 | 85 | 0.434 |

Table IV Contact Angle of PP Film with Distilled Water, Grafted at Various Photoinitiator Concentrations in the Presoaking Solution, [AM] = 0.5M, Acetone as Solvent

| PP Blown Film without Additive | | | | | | PP Blown Film with Additive | | | | | |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|-----------------------------|-------------|-------------|-------------|-------------|-------------|
| [BP] = 0.1M | | [BP] = 0.2M | | [BP] = 0.3M | | [BP] = 0.1M | | [BP] = 0.2M | | [BP] = 0.3M | |
| Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) |
| 0 | 90 | 0 | 91 | 0 | 91 | 0 | 91 | 0 | 89 | 0 | 90 |
| 4 | 55 | 4 | 59 | 5 | 32 | 4 | 21 | 4 | 29 | 4 | 41 |
| 7 | 38 | 7 | 41 | 9 | 28 | 7 | 35 | 7 | 24 | 7 | 42 |
| 11 | 46 | 10 | 39 | 13 | 33 | 10 | 32 | 9 | 26 | 9 | 36 |
| 15 | 50 | 13 | 40 | 17 | 36 | 15 | 46 | 12 | 34 | 12 | 34 |
| 18 | 54 | 17 | 41 | 19 | 49 | 19 | 39 | 16 | 32 | 17 | 44 |
| 28 | 67 | 32 | 51 | 35 | 63 | 33 | 45 | 32 | 55 | 32 | 53 |
| 63 | 69 | 70 | 68 | 65 | 63 | 69 | 64 | 69 | 44 | 68 | 50 |
| 96 | 82 | 115 | 76 | 100 | 78 | 100 | 61 | 106 | 59 | 95 | 65 |
| 157 | 72 | 164 | 76 | 148 | 78 | 143 | 63 | 150 | 67 | 146 | 69 |

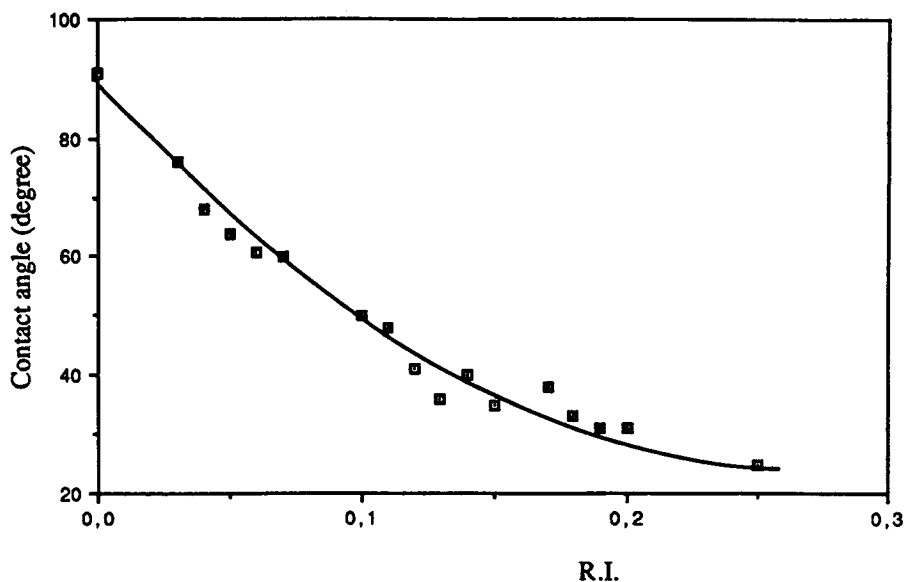
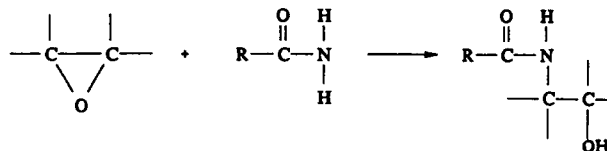


Figure 8 Plots of contact angle of grafted PP film with distilled water versus RI of ESCA lines N_{1s}/C_{1s} .

According to the results obtained in Table III, a plot of relative intensity of ESCA lines N_{1s}/C_{1s} versus adhesion of PP tape film to epoxy resin is made in Figure 12. When irradiation time is 9–14 sec, and $[AM] = 0.8\text{--}1.3M$ in the presoaking solution, the adhesion of grafted PP tape film surface to epoxy resin is 3–4 times higher than that of ungrafted film. We know from the ESCA measurements that the PP surface is grafted with AM monomer. The amide functional groups react easily with epoxide to form chemical bonds. The increment of adhesion of

grafted PP tape film surface is interpreted due to this chemical bond.



It is apparent that the curve in Figure 12 levels off when the RI of ESCA lines is about 0.15. This evidence suggests that only a quite thin grafted layer (maybe less than 50\AA) can react with epoxy groups and contribute to adhesion. In other words, modification of surface properties probably only needs an extremely thin grafted layer on the surface. Heavy grafting seems to have no further effect on the adhesion.

In conclusion, all four measurements—RI of ESCA lines, contact angle, dye adsorption, and adhesion to epoxy resin—have indicated that chemical photografting definitely occurs on the surface of PP film in our continuous presoaking process with 7–10 sec irradiation time.

Effect of Various Photoinitiator Concentrations in the Presoaking Solution

The RI of ESCA lines at various BP concentrations in the presoaking solution are shown in Figures 13–15. The general shape of the curves is similar to those shown in our earlier papers.^{16–18} The interpretation of the “shoulder” that appears in some

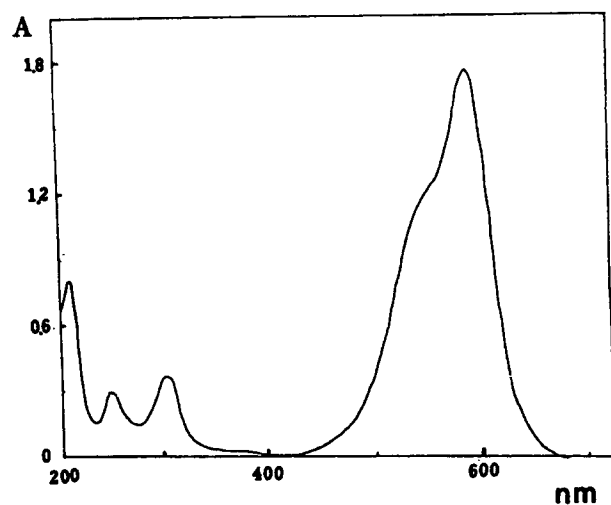


Figure 9 UV absorption spectrum of crystal violet indicator in aqueous solution.

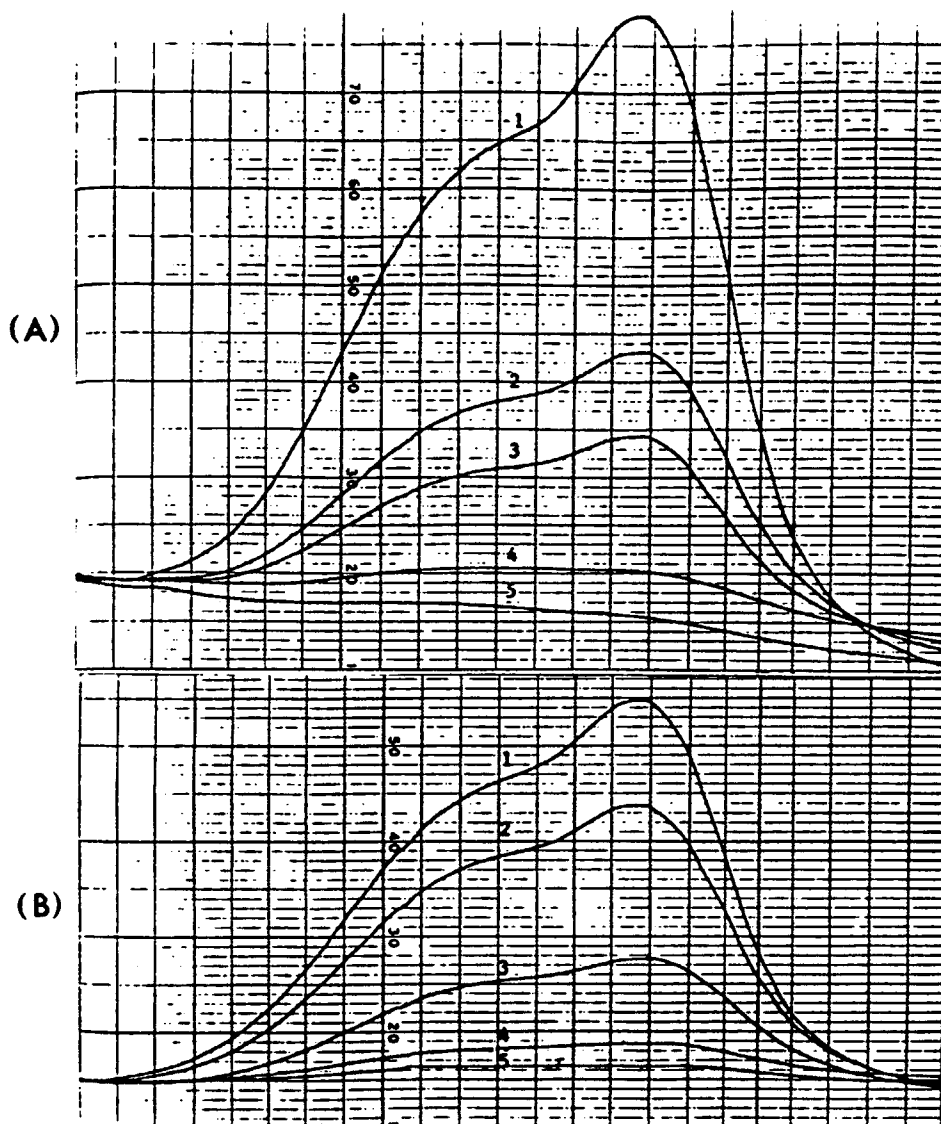


Figure 10 UV absorption spectra of grafted PP film dyed by crystal violet indicator. Irradiation time: 10 sec in 1, 2, 3, 4 in A, B; 0 sec in 5. Presoaking solution: $[BP] = 0.2M$, $[AM] = 1.3, 0.8, 0.5, 0.2M$ in 1, 2, 3, and 4, respectively. Acetone as solvent. PP film: blown film with additives (A), blown film without additive (B).

curves is the same as before, i.e., grafting of monomer and initiator from the vapour phase at prolonged irradiation. The effects of BP concentration seemed to be related to the type and processing of the PP film and consistent conclusions that one BP concentration is the best for all three types of PP film has not been found. There are some unknown factors that affect the results obtained. However, the modification of the PP surface by grafting has been achieved no matter which BP concentration is used. Tables IV and V show that the contact angle with

distilled water of PP blown and tape film decreased $45-60^\circ$ and adhesion of PP tape film to epoxy resin increased 3-4 times after about 10 sec irradiation time in grafting.

Effect of Various Solvents of Ketone

The solvent effects on the photografting are rather drastic, as shown in Tables VI and VII and Figures 16-18. The shape of the curves in Figures 16-18 is similar to those of our previous papers and the in-

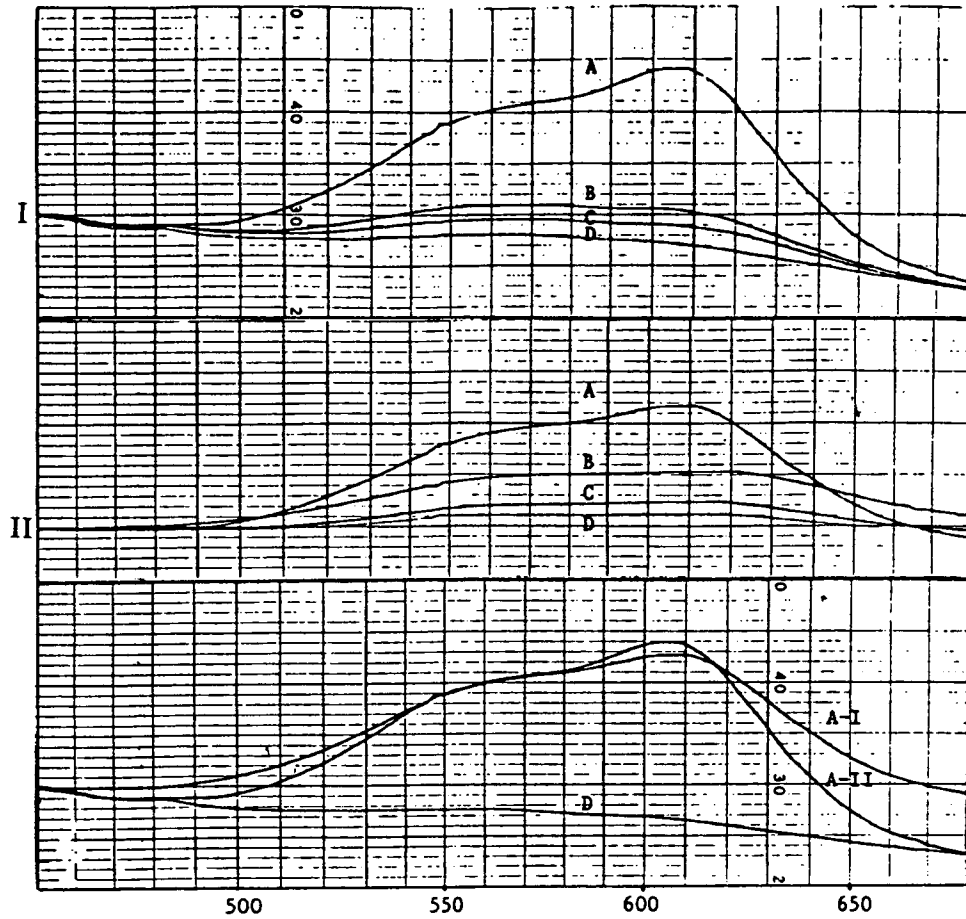


Figure 11 UV absorption spectra of grafted PP film dyed by crystal violet indicator. Irradiation time: 10 sec in A, B, C; 0 sec in D. Presoaking solution: [BP] = 0.2M, [AM] = 0.5M. Solvent: A, acetone; B, MEK; C, MPK. PP film: I, blown film with additive; II, blown film without additive.

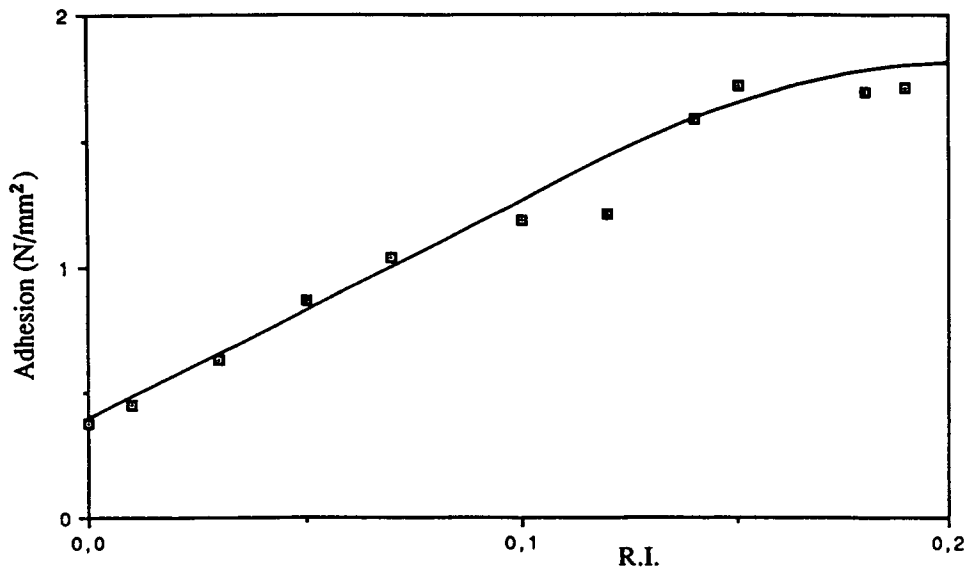


Figure 12 Plots of adhesion of grafted PP tape film to epoxy resin versus relative intensity of ESCA lines N_{1s}/C_{1s} .

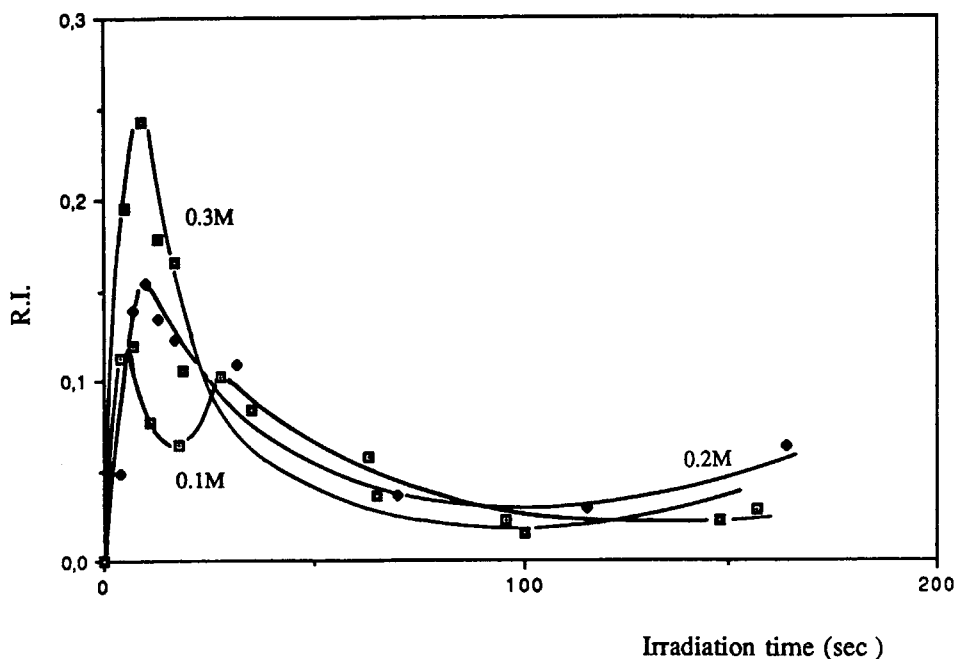


Figure 13 Effect of BP concentrations on photografting of PP blown film without additive, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, acetone as solvent.

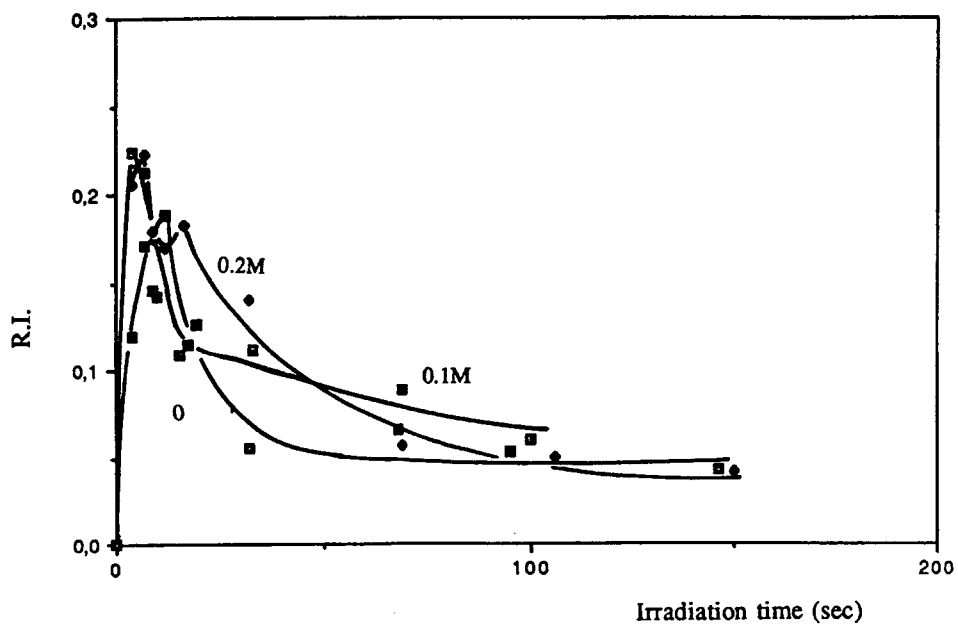


Figure 14 Effect of BP concentrations on photografting of PP blown film with additives, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, acetone as solvent.

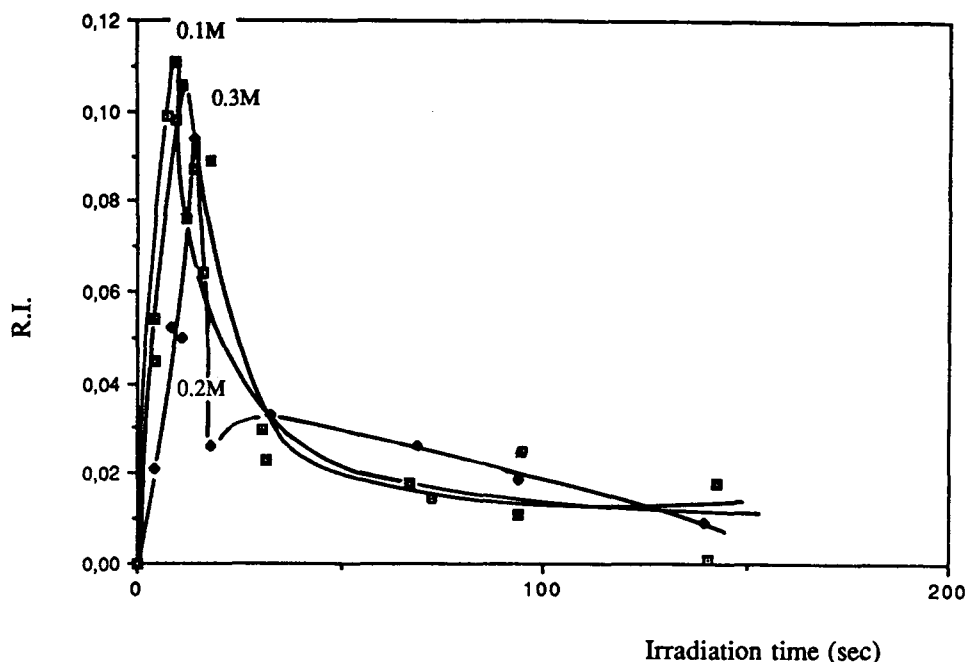


Figure 15 Effect of BP concentrations on photografting of PP tape film with additives, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, acetone as solvent.

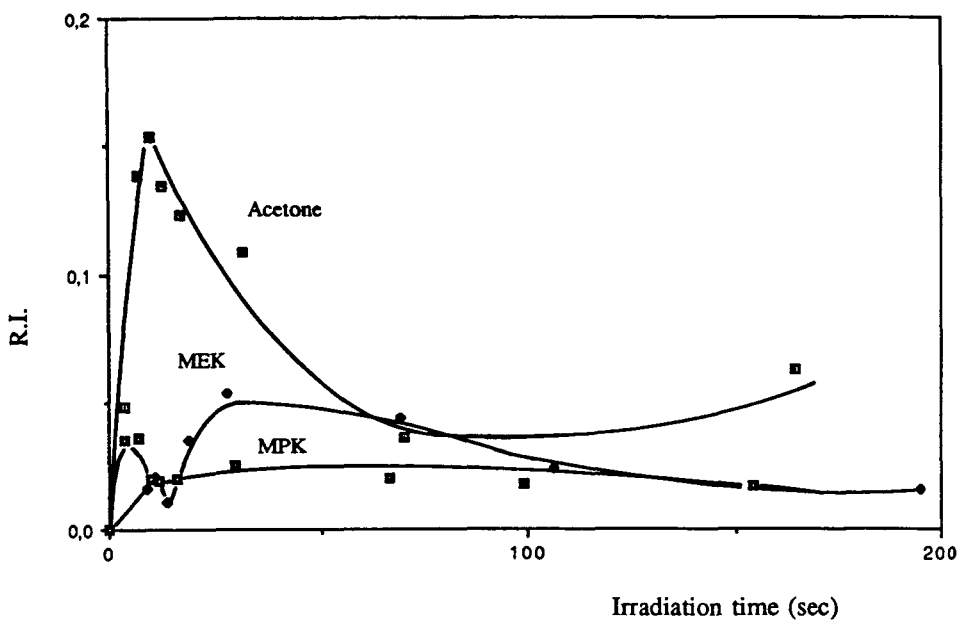


Figure 16 Effect of solvent on photografting PP blown film without additive, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, $[BP] = 0.2M$.

terpretation of the "shoulder" is the same as before. Figure 11 (a) and 11 (b) show dyeability differences of the PP blown film grafted with various ketones as solvents. Apart from the chemical effects of sol-

vents as hydrogen donors in the initiation and physical effects of solvents as UV light absorber, the interaction of solvent with the PP film should be considered here. The ketones are wetting the polymer

Table V Contact Angle of PP Tape Film with Distilled Water and Adhesion to Epoxy Resin, Film Grafted at Various BP Concentrations in the Presoaking Solution, Acetone as Solvent

| [AM] = 0.5M, [BP] = 0.1M | | | [AM] = 0.5M, [BP] = 0.2M | | | [AM] = 0.5M, [BP] = 0.3M | | |
|--------------------------|-------------|-------------------------------|--------------------------|-------------|-------------------------------|--------------------------|-------------|-------------------------------|
| Time (s) | CA (degree) | Adhesion (N/mm ²) | Time (s) | CA (degree) | Adhesion (N/mm ²) | Time (s) | CA (degree) | Adhesion (N/mm ²) |
| 0 | 91 | 0.384 | 0 | 90 | 0.282 | 0 | 91 | 0.384 |
| 4 | 54 | 0.971 | 4 | 72 | 0.499 | 4 | 65 | 0.868 |
| 7 | 41 | 1.223 | 8 | 58 | 0.887 | 9 | 47 | 1.110 |
| 9 | 39 | 1.249 | 11 | 53 | 0.823 | 11 | 42 | 1.194 |
| 12 | 50 | 1.128 | 14 | 41 | 1.197 | 14 | 50 | 1.133 |
| 16 | 41 | 1.001 | 18 | 61 | 0.707 | 18 | 51 | 1.143 |
| 31 | 62 | 0.724 | 33 | 45 | 0.820 | 32 | 62 | 0.564 |
| 73 | 75 | 0.477 | 69 | 68 | 0.610 | 67 | 73 | 0.537 |
| 95 | 76 | 0.550 | 94 | 74 | 0.611 | 94 | 80 | 0.494 |
| 140 | 81 | 0.425 | 139 | 81 | 0.431 | 142 | 74 | 0.486 |

Table VI Contact Angle with Distilled Water on PP Film, Grafted with Presoaking Solution

| PP Blown Film without Additive | | | | | | PP Blown Film with Additives | | | | | |
|--------------------------------|-------------|----------|-------------|----------|-------------|------------------------------|-------------|----------|-------------|----------|-------------|
| Acetone | | MEK | | MPK | | Acetone | | MEK | | MPK | |
| Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) | Time (s) | CA (degree) |
| 0 | 91 | 0 | 91 | 0 | 91 | 0 | 91 | 0 | 91 | 0 | 91 |
| 4 | 59 | 4 | 78 | 4 | 64 | 4 | 29 | 4 | 56 | 4 | 70 |
| 7 | 41 | 9 | 72 | 7 | 62 | 7 | 24 | 8 | 55 | 7 | 66 |
| 10 | 39 | 11 | 69 | 10 | 70 | 9 | 26 | 11 | 54 | 11 | 60 |
| 13 | 40 | 14 | 79 | 12 | 71 | 12 | 34 | 14 | 48 | 14 | 43 |
| 17 | 41 | 19 | 75 | 16 | 74 | 16 | 32 | 22 | 51 | 22 | 31 |
| 32 | 51 | 28 | 57 | 30 | 73 | 32 | 55 | 35 | 37 | 32 | 64 |
| 70 | 68 | 69 | 66 | 66 | 72 | 69 | 44 | 69 | 59 | 74 | 75 |
| 115 | 76 | 106 | 73 | 99 | 77 | 106 | 59 | 97 | 55 | 94 | 74 |
| 164 | 76 | 195 | 77 | 154 | 77 | 150 | 67 | 153 | 72 | 152 | 79 |

[BP] = 0.2M, [AM] = 0.5M.

Table VII RI of ESCA Lines N_{1s}/C_{1s}, Contact Angle with Distilled Water and Adhesion to Epoxy Resin of Grafted PP Tape Film with Additives, Presoaking Solution in Various Ketones

| Acetone | | | | MEK | | | | MPK | | | |
|----------|-------|-------------|-------------------------------|----------|-------|-------------|-------------------------------|----------|-------|-------------|-------------------------------|
| Time (s) | RI | CA (degree) | Adhesion (N/mm ²) | Time (s) | RI | CA (degree) | Adhesion (N/mm ²) | Time (s) | RI | CA (degree) | Adhesion (N/mm ²) |
| 0 | 0.000 | 90 | 0.282 | 0 | 0.000 | 91 | 0.312 | 0 | 0.000 | 90 | 0.294 |
| 4 | 0.021 | 72 | 0.499 | 4 | 0.031 | 73 | 0.770 | 4 | 0.021 | 68 | 0.469 |
| 8 | 0.052 | 58 | 0.887 | 10 | 0.033 | 72 | 0.760 | 8 | 0.031 | 64 | 0.688 |
| 11 | 0.050 | 53 | 0.823 | 11 | 0.032 | 74 | 0.768 | 10 | 0.027 | 66 | 0.557 |
| 14 | 0.094 | 41 | 1.197 | 13 | 0.030 | 69 | 0.721 | 13 | 0.021 | 63 | 0.490 |
| 18 | 0.026 | 61 | 0.707 | 17 | 0.038 | 65 | 0.876 | 17 | 0.024 | 68 | 0.543 |
| 33 | 0.033 | 45 | 0.820 | 31 | 0.005 | 79 | 0.466 | 32 | 0.037 | 70 | 0.758 |
| 69 | 0.026 | 68 | 0.610 | 71 | 0.001 | 85 | | 65 | 0.015 | 77 | |
| 94 | 0.019 | 74 | 0.611 | 94 | 0.001 | 88 | | 89 | 0.010 | 82 | |
| 139 | 0.009 | 81 | 0.431 | 141 | 0.001 | 84 | | 138 | 0.019 | 77 | |

[AM] = 0.5M, [BP] = 0.2M.

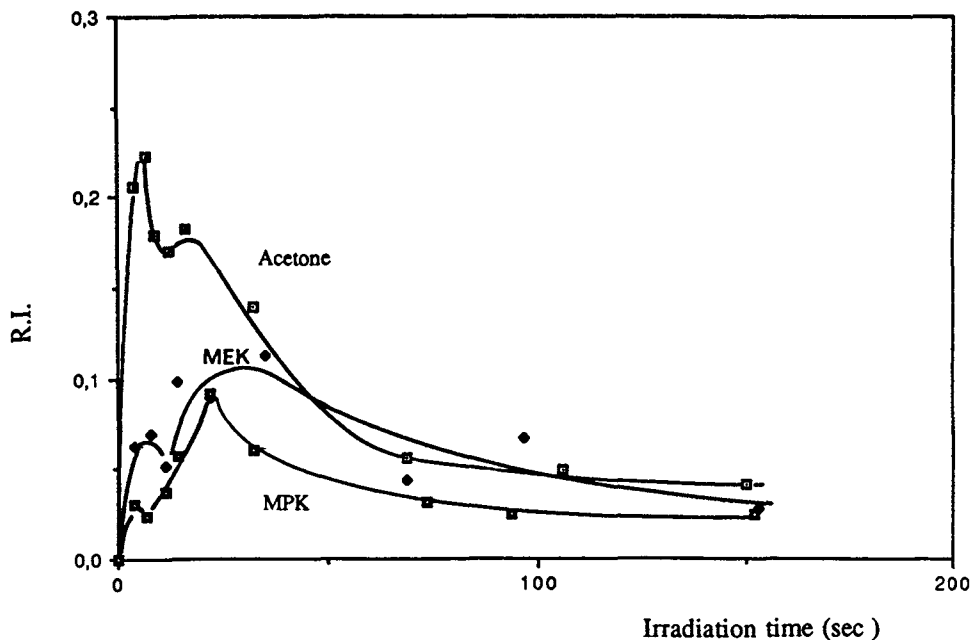


Figure 17 Effect of solvents on photografting of PP blown film with additive, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, $[BP] = 0.2M$.

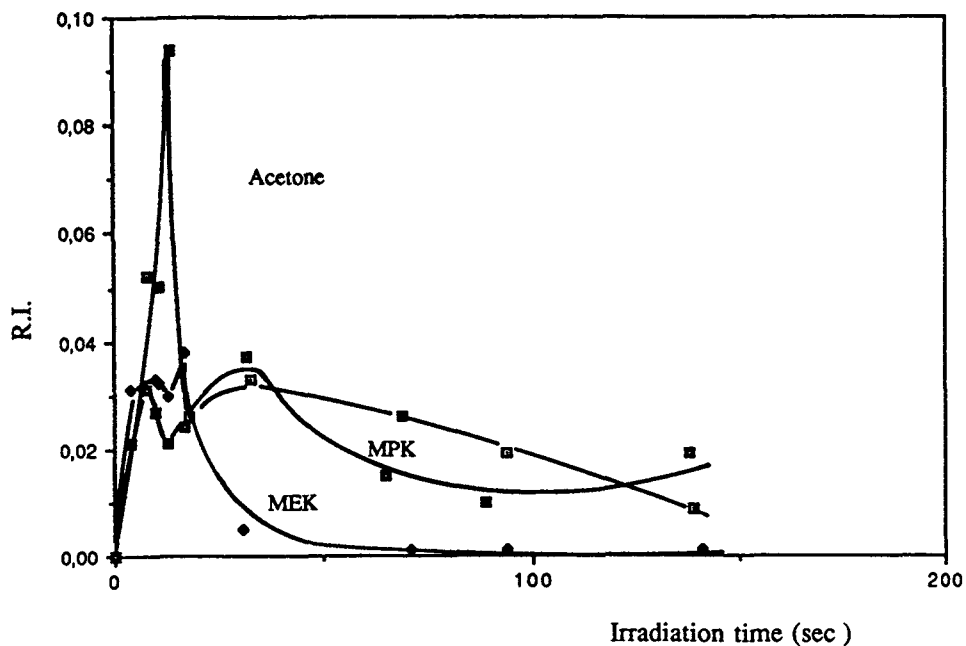


Figure 18 Effect of solvents on photografting of PP tape film with additive, measured as RI of ESCA lines N_{1s}/C_{1s} . Presoaking solution: $[AM] = 0.5M$, $[BP] = 0.2M$.

surface. The film surface may be slightly swollen in contact with the solvent and efficient grafting is expected. This might be one of the reasons that acetone as solvent in grafting is better than MEK or MPK.

CONCLUSIONS

Polypropylene film, with and without stabilizing additives, can be efficiently photografted on the sur-

face by presoaking in a ketone solution containing benzophenone and acrylamide and UV irradiation for short times (7–10 sec). After extracting the homopolymer formed in the surface, the relative intensity of the ESCA lines N_{1s}/C_{1s} increased from 0 to 0.20, the contact angle with distilled water decreased from 90 to 30°, the dye adsorption increased clearly, and the adhesion to Araldite epoxy resin increased 3–4 times compared with those of ungrafted PP tape film.

Stabilizing additives in the PP film has no measurable effect on the photografting, indicating that the additives do not migrate to the film surface to a measurable extent. The photografting process may, therefore, have applications for commercial modification of PP film. The AM concentration in the presoaking solution has a strong effect on the grafting yield, and 0.5–1.3M AM in the presoaking solution is recommended. The effect of measured concentration of BP is favourable for high grafting yields. Acetone is the best solvent among the three ketones used (acetone, MEK, MPK).

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