

Research Article

Modification of Poly(vinyl chloride) by *N*-Phenyl Itaconimides for the Improvement of Its Thermal Stability

Asma M. Elsharif , Azza A. Al-Ghamdi, and Abir S. Abdel-Naby 

Chemistry Department, College of Science, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, 31441 Dammam, Saudi Arabia

Correspondence should be addressed to Abir S. Abdel-Naby; aabdelnaby@iau.edu.sa

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Poly(vinyl chloride) (PVC) is modified by *N*-phenyl itaconimide derivatives (*N*-(RPh)IM) as modifying agents or graft comonomers. The resulting modified polymers or graft copolymers were characterized using FTIR and UV/Vis spectrophotometry. The thermal properties of the modified polymers were investigated using thermogravimetry (TGA), which revealed that the synthesized polymers exhibited high thermal stability, as shown from the value of their initial decomposition temperatures and the percentage of weight loss at high temperatures. The polymer modified by 4-bromo itaconimide exhibited the most thermal stability. A mechanism for the modification reaction and the graft copolymerization of PVC was suggested.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most produced polymers. It is mainly used in various plastic applications.

Despite possessing the advantage of being a low-cost polymer, PVC suffers from poor heat stability. While the molding temperature needed for most PVC products exceeds 180°C, the polymer starts to degrade at 120°C. Thus, the polymer should be thermally stabilized before the molding process. The thermal degradation leads to the evaluation of HCl gas and formation of conjugated polyenes [1], causing discoloration of the polymer. Thus, labile sites, tertiary and allyl chlorine atoms, should be replaced by more stable groups before the molding process. This occurs through chemical modification [2, 3], graft copolymerization [2, 4, 5], or simply adding various thermal stable compounds [6, 7].

Itaconimide derivatives were previously used as thermal additives for PVC [8, 9], but the additives technique is not considered as an effective method for the stabilization since the stable additives act as a physical protector on the surface layer of the polymer only. It does not prevent the formation of HCl and the polyenes inside the polymeric matrix.

In the present work, chemical modification and graft copolymerization are used to synthesize stable PVC,

free from labile sites and capable of withstanding high temperatures.

2. Materials and Methods

2.1. Materials and Chemicals. Poly(vinyl chloride) (PVC) was obtained from the Sabcic company with a *k* value of 67 and itaconic anhydride 98% from Acros. Freshly distilled tetrahydrofuran (THF) was used, and cyclohexanone (99.8%) was purchased from Acros.

2.2. Synthesis of Itaconimide Derivatives. All *N*-(substituted phenyl)itaconimide derivatives (*N*-(RPh)IM) were prepared by two steps described by Adam [6]. In the first step, 1 mol of itaconic anhydride was dissolved in dry diethyl ether and then, 1 mol of the primary amine dissolved in the same solvent was slowly added to the itaconic anhydride at 0–5°C for 3 hours. The resulted acid *N*-(substituted phenyl)itaconic acid was filtered, washed, and dried. The following step was cyclization which occurred by adding acetic acid anhydride and fused sodium acetate in a steam bath for 30 minutes. The resulted monomer was crystallized from aqueous ethanol. Table 1 shows the melting points of prepared itaconimide derivatives.

TABLE 1: Melting points of various *N*-(halo phenyl)itaconimides.

| <i>N</i> -(phenyl)itaconimide derivatives | Melting point (°C) |
|--|--------------------|
| <i>N</i> -(phenyl)itaconimide [<i>N</i> -Ph IM] | 112-113 |
| <i>N</i> -(4-chloro phenyl)itaconimide [<i>N</i> -(4-ClPh)IM] | 131-132 |
| <i>N</i> -(4-bromo phenyl)itaconimide [<i>N</i> -(4-BrPh)IM] | 134-135 |

2.3. Preparation of Modified Polymers. The modified polymer was prepared according to the Abdel Naby method [2, 3]. 64 mmol of PVC was dissolved in 1 L of cyclohexanone. 50 mmol of the itaconimide was added to PVC solution stirred, at 60°C, under the nitrogen atmosphere. The resulted polymer was obtained by precipitating the polymer mixture in cold methanol, filtered, and then purified by the Soxhelt system using hot methanol. The polymer was dried under vacuum.

2.4. Preparation of Graft Copolymer. The graft copolymer was prepared by adding benzoyl peroxide (initiator) to the dissolved PVC solution in THF, at 50°C, under the nitrogen atmosphere for 10 minutes. Afterwards, the monomer solution was injected to the reaction medium, allowing the grafting process to occur for two hours. The product was precipitated in cold ethanol, purified using the Soxhlet system, and then dried in vacuum oven at 40°C [2, 9]. The graft percentage was investigated by the following equation:

$$\%G = \left(\frac{W_g - W_o}{W_o} \right) \times 100, \quad (1)$$

where W_o is the weight of native PVC and W_g is the weight of polymer after the graft process.

2.5. Preparation of the Poly(vinyl chloride) Films. 1 g of the polymer sample was dissolved in THF and poured onto a dry Petri dish, and then the resulted film was dried, in vacuum oven, at 70°C.

2.6. Evaluation of the Degradation Process. Evaluation of the stabilizing efficiency was carried out by measuring the rate of dehydrochlorination by the continuous potentiometric determination of the hydrogen chloride evolved at 180°C in air. A detailed description of this method was given by Vymazal et al. [10].

A digital pH meter (potentiometer), Type HI 9321 PH (HANNA Instruments, Germany), of accuracy 1 digit 1/40.1 mV was used. It was connected to a silver electrode for the potentiometric measurements. The results reported are the average of three replicates in each case.

2.7. Investigation of the Discoloration of the Thermally Degraded Samples. UV/visible spectrophotometry was used to determine the formation of polyenes (extent of discoloration) as indication of the degradation process. A PerkinElmer Lambda 4 device was used. Constant concentration solutions in all samples were prepared.

2.8. Thermogravimetry (TG). TG data were obtained by Shimadzu TGA-50H under the N_2 atmosphere at a heating rate of 10°C/min from room temperature to 500°C.

3. Results and Discussion

3.1. Characterization of the Modified Copolymer

3.1.1. UV/Vis Spectroscopy. Figure 1 shows the UV/Vis spectrum of modified PVC by *N*-(4-BrPh)IM. The spectrum displayed new two peaks around 330 nm and 390 nm. Since PVC does not absorb in the UV/Vis region, these two peaks confirmed the modification of the polymer by the suggested comonomers.

3.1.2. IR Spectroscopy. Figure 2 shows the IR spectroscopy of modified PVC by 4-(BrPh)IM. The IR spectrum showed the following peaks:

- (i) The C=C stretching band at 1637 cm^{-1} corresponding to the stabilizer moieties.
- (ii) The peak corresponding to C=O stretching appears at 1709 cm^{-1} . This peak was shifted to the lower wavenumber as a result of the delocalization of electrons between double bond and carbonyl groups ((Scheme 1), equation 1(a), structure A).
- (iii) Broad peak at 3400 cm^{-1} indicating the formation of enolic form of stabilizer moieties (Scheme 1 (A)).

Figure 3 displays the IR spectra of modified PVC before and after 2 hours of exposure to molding temperature 180°C in air. The result revealed the following observations:

- (i) Absence of ethylenic bond C=C which indicated the participation of the double bond in the stabilization process
- (ii) Also, the presence of the C=O peak at 1728 cm^{-1} , unshifted to the lower wavenumber as in case of the ungrafted copolymer, confirmed the consumption of the ethylenic bond in the stabilization reaction which prohibited the conjugation of double bond with the carbonyl group

Moreover, the disappearance of the broad peak at 3400 cm^{-1} confirmed the absence of enol form as a result of the participation of the C=C bond in the stabilization process.

Following up the discoloration of the modified polymer (PVC/4(BrPh)IM) with the degradation time, at 180°C, gradual increase in the discoloration of the sample occurred with thermal degradation time, till 35 minutes. Conversely, increasing the time of degradation (>35 min) lightness of the degraded sample coloration occurred (Table 2) which confirmed the possibility of the occurrence of the Diels-Alder reaction (Scheme 1, equation 1(b)).

3.2. Thermal Gravimetry (TG) of Modified PVC. Regardless of the molding process, an essential target of this work was to produce PVC capable to withstand high temperature. To investigate the thermal behavior of the synthesized modified

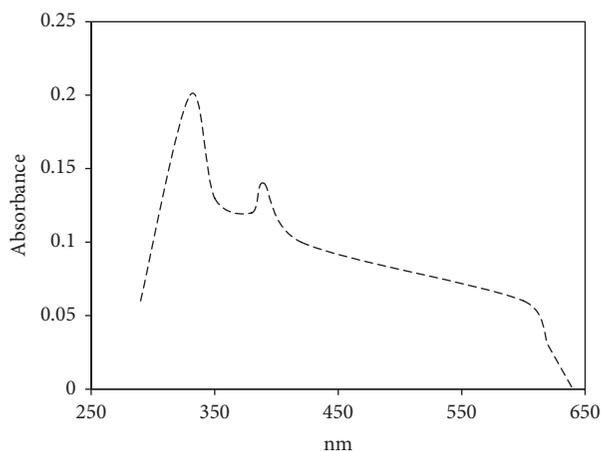


FIGURE 1: UV spectrum of PVC modified by *N*-(4-BrPh)IM.

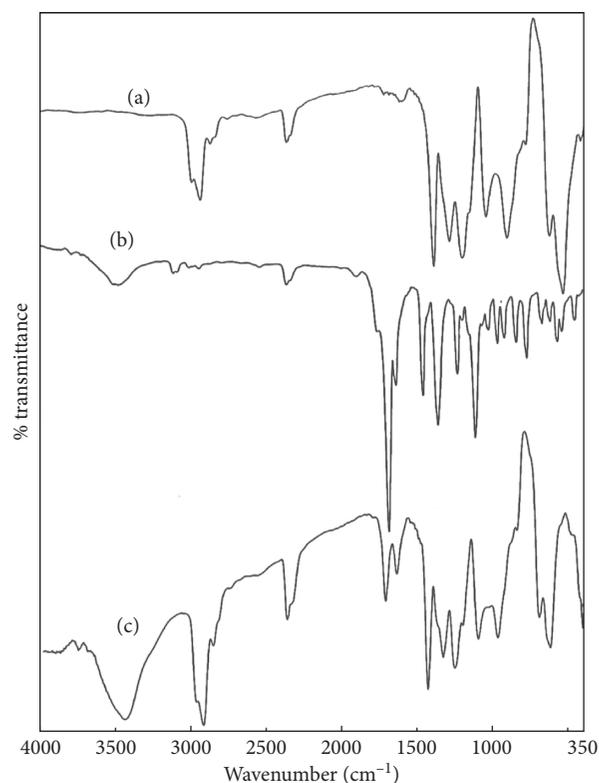


FIGURE 2: FTIR spectra of PVC modified by *N*-(4-BrPh)IM (c) as compared to *N*-(4-BrPh)IM monomer (b) and PVC (a).

polymer, at high temperature (up to 500°C), TG technique was used.

Figure 4 and Table 3 show the thermal behavior of the modified copolymers. PVC/4-(BrPh)IM exhibited the highest thermal stability, as shown from T_0 values ($T_0 = 294^\circ\text{C}$) and the total weight loss, at 500°C (59%). PVC/4-(ClPh)IM exhibited less T_0 value 283°C but still exhibited higher thermal stability than unmodified polymer ($T_0 = 247^\circ\text{C}$).

3.3. Stabilization of PVC through Graft Copolymerization. In order to build a stabilizer polymeric in nature through the polymeric matrix to increase the thermal stability of the

polymer, the graft copolymerization was used. Before undergoing the graft copolymerization of PVC with the suggested itaconimide derivatives, the grafting parameters were studied to determine the optimum conditions for the grafting process.

3.4. Factors Affecting Graft Copolymerization

3.4.1. Effect of Initiator Concentration. The study of the effect of initiator concentration on the percentage of graft showed that the percentage of graft increased with the increase in the initiator concentration up to 1.5×10^{-2} mol/L, followed by remarkable decrease in the G% (Figure 5). This might be attributed to termination reactions of growing radicals by excess free radicals produced from initiator molecules [11, 12].

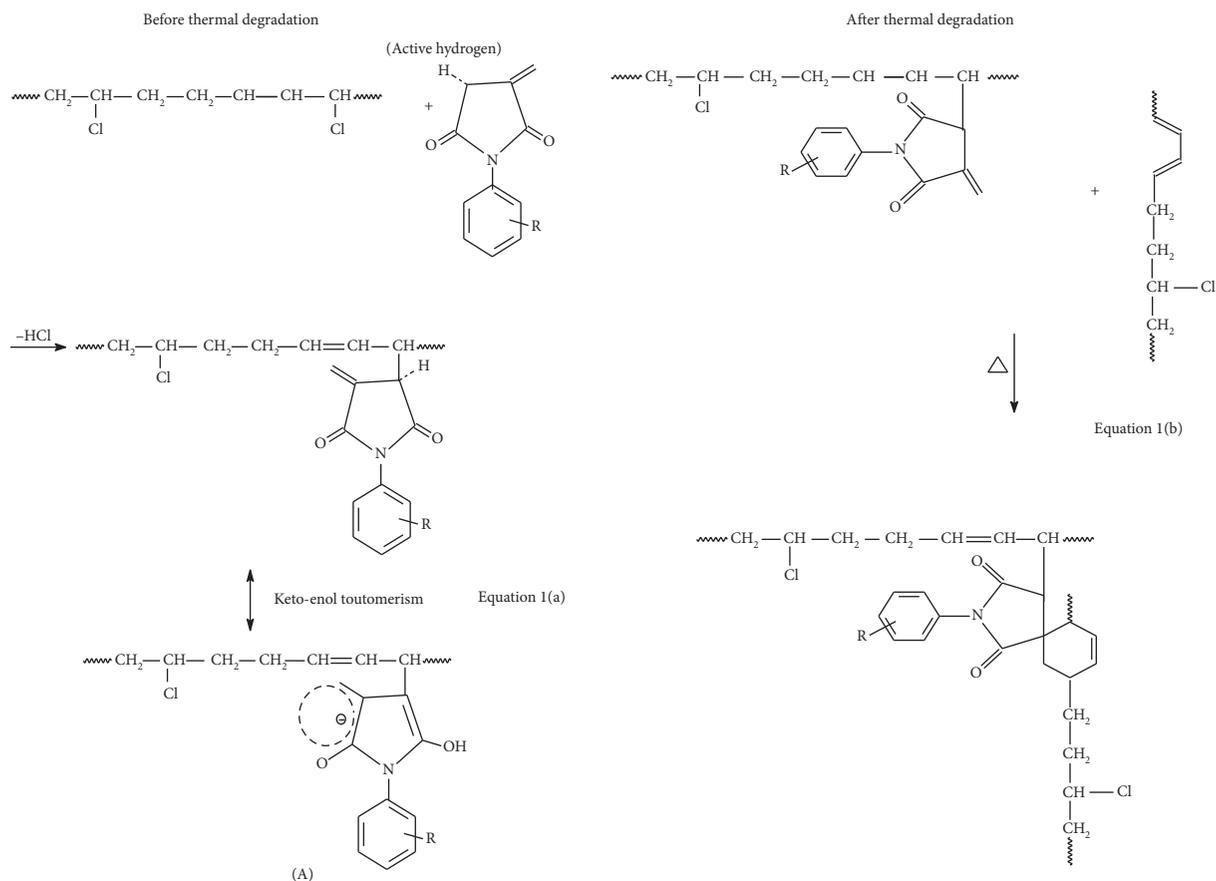
3.4.2. Effect of Monomer Concentration. Figure 6 indicates that increasing monomer concentration up to 3×10^{-1} mol/L led to an increase in the percentage of graft (17%) followed by slightly decrease in %G (15%) for 6×10^{-1} mol/L, and this might be attributed to the formation of the homopolymer [11].

3.4.3. Effect of Temperature. The study of the effect of temperature on %G showed that increasing reaction temperature led to slight gradual increase in %G till 50°C and then a sudden increase occurred up to %G = 22%; then, a constant percentage of graft was observed for the range 58°C to 68°C followed by a sharp decrease. This could be attributed to increase the chain termination reactions between monomer molecules and grafted chains or chain transfer reactions [12, 13] (Figure 7).

3.5. Characterization of the Grafted PVC Copolymer

3.5.1. IR Spectroscopy. The IR spectroscopy was the main tool used to characterize the structure of the graft copolymer. Figure 8 shows the IR spectrum of PVC-g-4(BrPh)IM. The spectrum involved the following:

- (i) Disappearance of the stretching band of C=C, corresponding to stabilizer moieties at 1660 cm^{-1} : this is attributed to the incorporation of double bond of comonomer in the graft process.
- (ii) Appearance of the strong band referred to the carbonyl group at 1713 cm^{-1} as compared to that of pure stabilizer: this is due to absence of resonance between C=O and ethylenic bond which was consumed in graft copolymerization.
- (iii) Appearance of the bending peak according to the aromatic ring (bending out of plane) at 820 cm^{-1} .
- (iv) In addition, Table 4 shows the effect of the thermal degradation at 180°C, in air, on the discoloration of PVC which was modified or grafted by 4-(BrPh)IM as compared to that of PVC. This deepness in color could be explained by consuming the



SCHEME 1: Suggested reaction mechanism representing the modification of poly(vinyl chloride) by *N*-phenyl itaconimide derivatives, before and after exposure to molding temperature 180°C, in air.

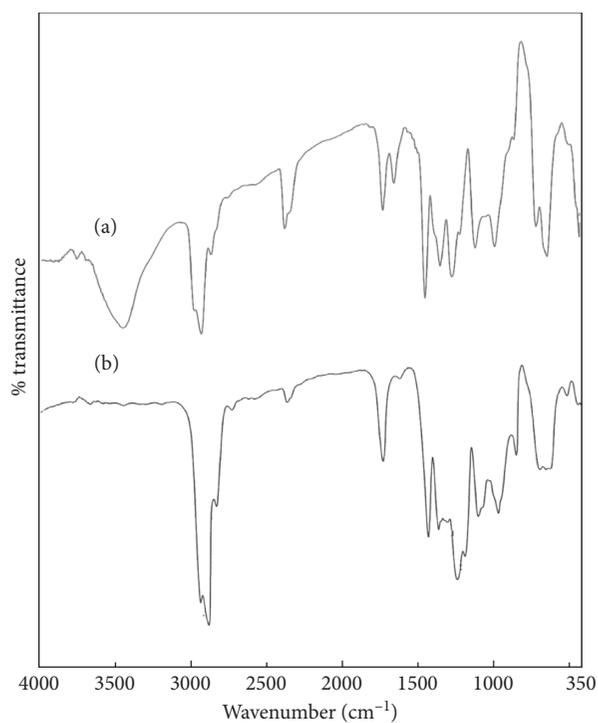


FIGURE 3: FTIR spectra of PVC modified by *N*-(4-BrPh)IM (a) before thermal degradation and (b) after thermal degradation, at 180°C, in air.

TABLE 2: Effect of thermal degradation at 180°C, in air, on the discoloration of the films of PVC modified by *N*-(4-BrPh)IM as compared to that of PVC.

| Time of degradation (min) | PVC | PVC modified by <i>N</i> -(4-BrPh)IM |
|---------------------------|--|--|
| 0 |  |  |
| 10 |  |  |
| 35 |  |  |
| 135 |  |  |

TABLE 3: Initial decomposition (T_0) and total weight loss percentage at 500°C of PVC and modified PVC by various itaconimide derivatives, under the nitrogen atmosphere.

| Polymeric sample | Initial decomposition temperature T_0 (°C) | Total weight loss (%) at 500°C |
|-----------------------|--|--------------------------------|
| PVC | 247 | -78 |
| <i>N</i> -(4-BrPh)IM | 294 | -59 |
| <i>N</i> -(4-ClPh)IM | 283 | -61 |
| <i>N</i> -PhIM | 255 | -70 |
| <i>N</i> -(4-MeOPh)IM | 264 | -67 |

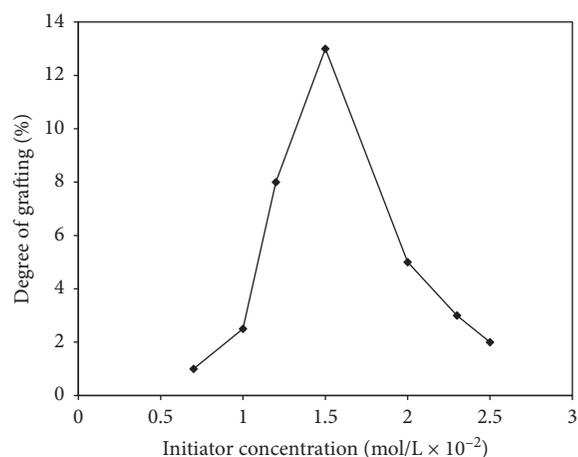


FIGURE 5: Effect of initiator concentration on the degree of grafting on PVC by *N*-PhIM. Monomer concentration ($3 \text{ mol/L} \times 10^{-1}$) at 60°C for 17 h.

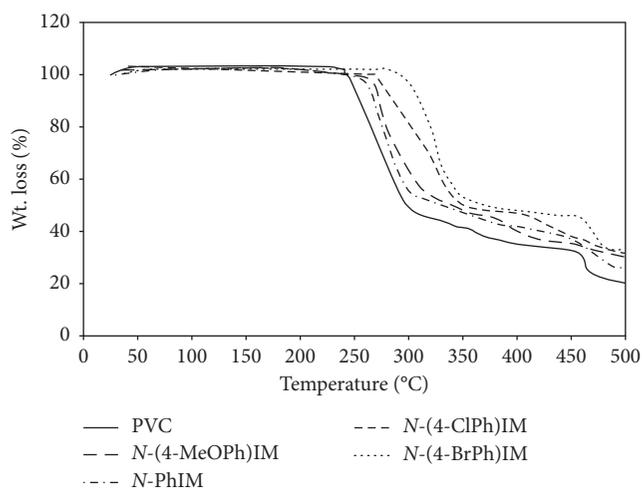


FIGURE 4: Thermal gravimetric analysis of PVC modified by various itaconimide derivatives as compared to PVC.

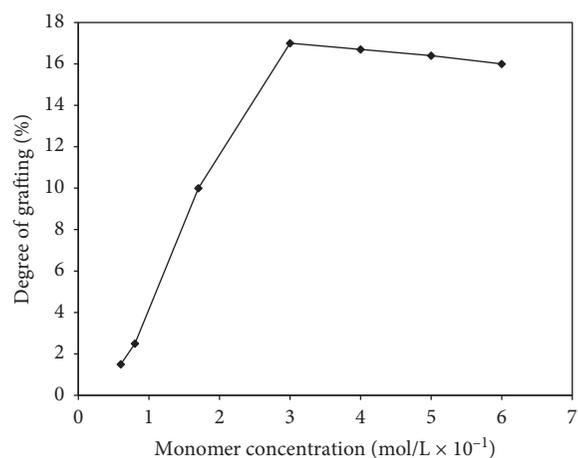


FIGURE 6: Effect of monomer concentration on the degree of grafting on PVC by *N*-PhIM. Initiator concentration of $1.5 \text{ mol/L} \times 10^{-2}$ at 60°C for 17 h.

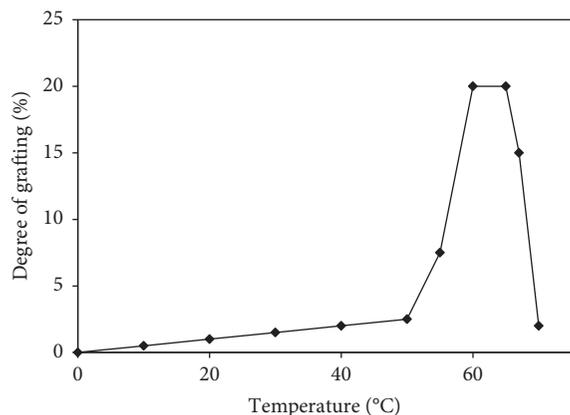


FIGURE 7: Effect of temperature on the degree of grafting on PVC by *N*-PhIM. Monomer concentration of $3 \text{ mol/L} \times 10^{-1}$; initiator concentration of $1.5 \text{ mol/L} \times 10^{-2}$ for 17 h.

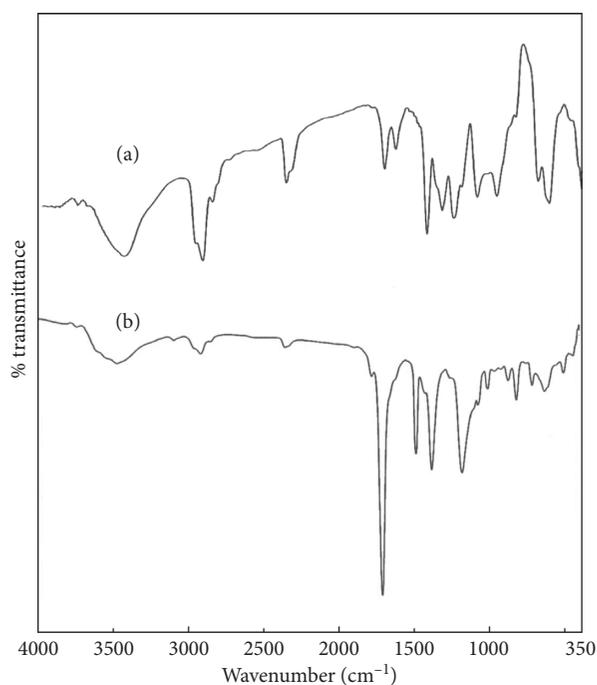


FIGURE 8: FTIR spectra of PVC stabilized by *N*-(4-BrPh)IM through (a) chemical modification and (b) graft copolymerization.

ethylenic bonds C=C by the grafting process; thus, no Diels–Alder reaction with polyene formed (Scheme 2).

3.5.2. Thermal Gravimetry (TG) of Grafted Copolymers. To compare the thermal behavior of the graft copolymer and PVC, the TG analysis was used. The results of the initial decomposition temperature values revealed that PVC-g-4-(BrPh)IM possessed higher thermal stability ($T_0 = 313^\circ\text{C}$) than PVC-g-4-(ClPh)IM ($T_0 = 278^\circ\text{C}$).

In addition, the values of total weight loss of grafted samples decreased to 50% for PVC-g-4-(BrPh)IM and 57%

TABLE 4: Effect of thermal degradation at 180°C , in air, on the discoloration of the PVC modified and grafted by *N*-(4BrPh)IM as compared to PVC.

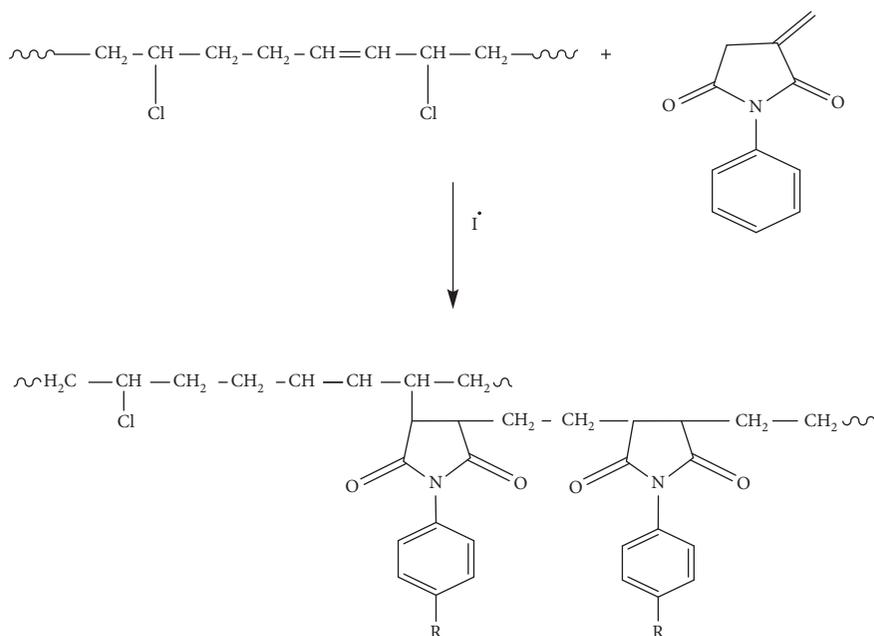
| Time of degradation (min) | PVC | PVC modified by <i>N</i> -(4-BrPh)IM | PVC grafted by <i>N</i> -(4BrPh)IM |
|---------------------------|-----|--------------------------------------|------------------------------------|
| 0 | | | |
| 10 | | | |
| 35 | | | |
| 135 | | | |

for PVC-g-4-(ClPh)IM as compared to that of pure PVC (78%) (Figure 9).

Table 5 shows the initial decomposition temperature (T_0) and total weight loss percentage, at 500°C , of grafted and modified PVC samples as compared to PVC. The data clarified that the graft copolymerization gave the polymer extra heat stability than the simply modification process.

The extra thermal stability of the grafted copolymers was observed from the higher T_0 value and lower weight loss percentage (Table 5). This might be due to the ability of the grafted branches which possessed the ability to wrap around the main chains, protecting them from the heat effect.

3.5.3. Determination of the Extent of Discoloration. Comparison between the extent of discoloration of the thermally degraded grafted copolymer and that of the modified polymer is illustrated in Figure 10. All samples were degraded for 2 hours in air at 180°C . The results indicated that graft and modification techniques could be used to inhibit the discoloration of PVC. The modified polymer (PVC/4(BrPh)IM) sample showed slight improvement as compared to the PVC grafted with the same monomer. This referred to the ability of the modified samples performing the Diels–Alder reaction through the ethylenic double bonds, while the graft copolymer could not since the double bonds were consumed in the graft copolymerization.



SCHEME 2: Suggested reaction mechanism representing the grafting of *N*-phenyl itaconimide onto poly(vinyl chloride) chains.

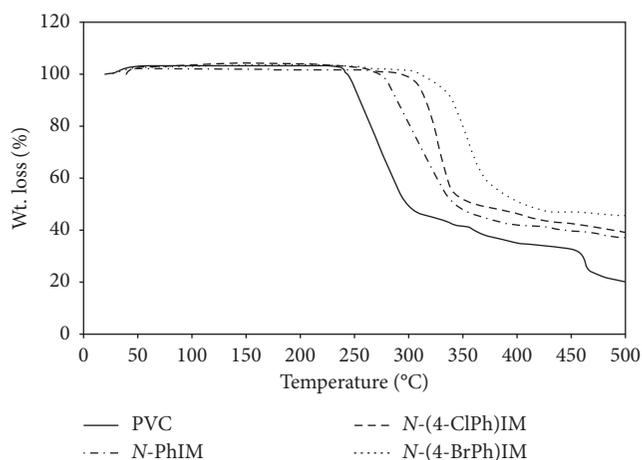


FIGURE 9: Thermal gravimetric analysis of PVC grafted by various itaconimide derivatives as compared to PVC. % of graft for samples 2–2.5%.

TABLE 5: Initial decomposition (T_0) and total weight loss percentage, at 500°C, of grafted and modified PVC as compared to PVC, under the nitrogen atmosphere.

| Polymeric sample | Initial decomposition temperature T_0 (°C) | Total weight loss (%) at 500°C |
|-------------------------------|--|--------------------------------|
| PVC | 247 | -78 |
| <i>N</i> -(4-BrPh)IM (modify) | 294 | -59 |
| <i>N</i> -(4-BrPh)IM (graft) | 313 | -50 |
| <i>N</i> -(4-ClPh)IM (modify) | 283 | -61 |
| <i>N</i> -(4-ClPh)IM (graft) | 298 | -57 |
| <i>N</i> -PhIM (modify) | 255 | -70 |
| <i>N</i> -PhIM (graft) | 278 | -60 |

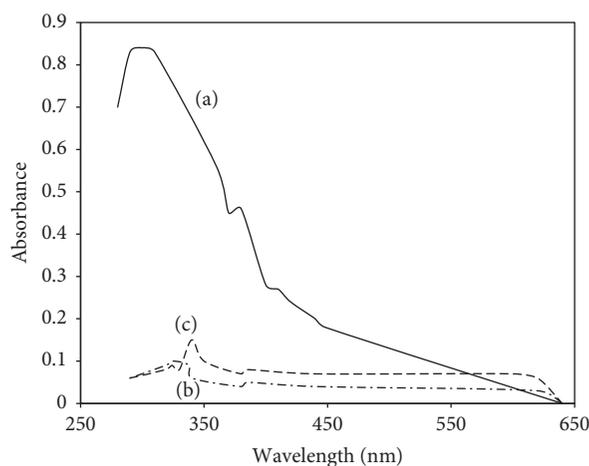


FIGURE 10: UV spectra of degraded (a) parent PVC, (b) PVC grafted by *N*-(4-BrPh)IM, and (c) PVC modified by *N*-(4-BrPh)IM samples, dissolved in THF (concentration 0.02 g·l⁻¹), at 180°C for 2 hours in air.

4. Conclusions

In order to improve thermal stability of PVC, itaconimide derivatives were used to prepare modified polymer and graft copolymers. The resulting products were characterized using IR and UV/Vis spectroscopy. Both techniques, modification reaction and graft copolymerization, led to thermally stable polymers as shown from their initial decomposition temperatures and weight loss percentages.

Moreover, both the grafted copolymers and modified polymers exhibited less degree of discoloration than parent PVC. Mechanisms for both modification and grafting copolymerization reactions confirmed that the modification reaction did not occur through the ethylenic bond, and they are consumed in the grafting process. The modified PVC by

4-bromoitaconimide exhibited the highest thermal stability. Thus, it is highly recommended to modify PVC using itaconimide derivatives, by chemical reactions or graft copolymerization, prior to the molding process.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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