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Photo-induced Charge-transfer and Photovoltaic Effect in a Composite Involving a Nonconjugated Conductive Polymer and C₆₀

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Photo-induced charge-transfer and resulting photovoltaic effect in a composite involving a *nonconjugated* conductive polymer, poly(β -pinene) and C₆₀ is reported. The photovoltaic cell was fabricated using indium-tin-oxide coated glass as one electrode and aluminum as the other, with poly(β -pinene)-C₆₀ composite film sandwiched in-between. A Nitrogen laser (325 nm) and an illuminant white-light-source (300–700 nm) were used and the photo-voltage produced was found to have a linear dependency on light intensity. The photoluminescence of poly(β -pinene) (at 360 nm) was quenched when C₆₀ was added to form the composite. Therefore, the photovoltaic effect is a result of excited-state electron-transfer from poly(β -pinene) to C₆₀.

Keywords: Photovoltaic effect, photo-induced charge-transfer, nonconjugated conductive polymer

1 Introduction

Organic polymers have attracted a great deal of interest in the area of photovoltaics. These materials show promising results and can serve as lower cost alternatives to inorganic photovoltaic materials (1–6, 8–10). The first two-layer organic photovoltaic system appears to have been reported in 1958 (4). Poly(p-phenylene vinylene) (PPV) has been widely studied in the research area of organic photovoltaic devices (1, 5). Reports have been made on photovoltaic devices based on polythiophene (6, 7). Composites involving conjugated organic polymers and electron acceptors have been widely studied for photovoltaics. Buckminsterfullerene, C₆₀ and its derivatives have been widely used in the area of photovoltaics since its discovery (8). Photo-induced electron-transfer between conjugated polymer and C₆₀ leading to photovoltaic effects have been investigated in detail (9, 10).

2 Experimental

2.1 Material and Methods

In this report, the photo-induced electron-transfer and resulting photovoltaic effect in a composite involving a *non-*

conjugated conductive polymer and fullerene will be discussed. Such effect involving a nonconjugated conducting polymer is being reported for the first time. It was established in 1988 by Thakur that conjugation is not a prerequisite for a polymer to be electrically conducting. Certain nonconjugated polymers with at least one double bond in their repeat unit can be electrically conducting upon doping with electron acceptors (11). Poly(β -pinene) is a recent addition to the class of nonconjugated conducting polymer. Figure 1 shows the molecular structure of poly(β -pinene). Upon doping with iodine, the electrical conductivity of this polymer goes up by more than ten orders of magnitude (12). Formation of radical cations upon doping and charge-transfer from the isolated double-bond and the dopant is responsible for the enhancement of conductivity. In this report, we discuss results of interaction of C₆₀ with the isolated double-bonds of poly(β -pinene).

The solutions of composites were prepared by dissolving weighed quantities of poly(β -pinene) and C₆₀ in toluene. Composites having different concentrations of C₆₀ ranging from 0% to 8% by weight were prepared. The films of these composites were cast on a glass slide under normal environmental conditions. Figure 2 shows the optical micrographs of these films. It was observed that the composite films having about 4% C₆₀ by weight or less were more homogeneous compared to films having a higher weight percent of C₆₀. This is because the solution is saturated when the C₆₀ added is more than 4% by weight. As a consequence, the film with 8% by weight of C₆₀ is less homogeneous. The

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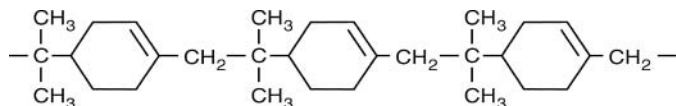


Fig. 1. Molecular structure of poly(β -pinene).

optical absorption, photoluminescence spectra and photo-voltaic effects in these composite films were measured for different concentrations of C_{60} .

3 Results and Discussion

Thin films of the composites were cast on glass substrates and the absorption spectra of the films were studied. Pristine poly(β -pinene) has an absorption peak at about 270 nm. The optical absorption spectra of the composites formed by poly(β -pinene) and C_{60} at different concentrations is shown in Figure 3. The composites show two distinct peaks, one at ~ 270 nm and the other at ~ 335 nm. The inset in Figure 3 shows the absorption spectrum of C_{60} . The peak at 270 nm observed in the composite is due to poly(β -pinene) and C_{60} , while the peak at 335 nm is due to C_{60} alone. The intensity of the absorption peak for the composite film increases with increase in the concentration of C_{60} (by % weight). As shown in the Figure 3, the bottom most spectrum corresponds to the composite with 0% C_{60} by weight (pristine poly(β -pinene)). The spectrum above it corresponds to the composite having 1% C_{60} by weight. The top-most spectrum corresponds to the composite having 8% C_{60} by weight. As these spectra show, the absorption characteristics of poly(β -pinene) does not change in association with C_{60} since no new peak appears in the composite spectra other than those of the components. Therefore, no charge-transfer between the polymer and C_{60} occurs at the ground state.

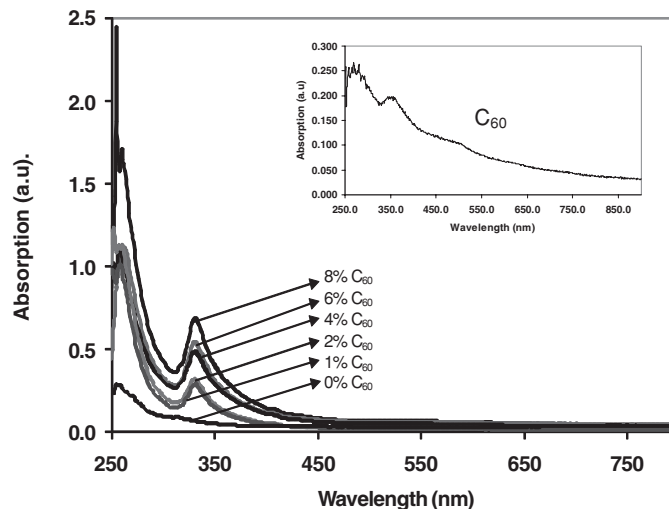


Fig. 3. Optical absorption spectra of the composites involving poly(β -pinene) and different weight percents of C_{60} . The inset shows the absorption spectrum of C_{60} alone.

The photoluminescence of the composite films has been studied (Figure 4) using Perkin Elmer LS-55 spectrometer. As shown in the inset of Figure 4, pristine poly(β -pinene) has an emission peak at 360 nm for an excitation wavelength of 280 nm (12). The photoluminescence is quenched in the composite involving poly(β -pinene) and C_{60} . This is because the photo-excited electron in poly(β -pinene) is transferred to C_{60} leading to no luminescence. These results confirm photo-induced charge-transfer in the composite involving poly(β -pinene) and C_{60} .

Photovoltaic cells used in the report were formed by sandwiching the composite film between two electrodes. Aluminum coated glass slide was used as one electrode and indium-tin-oxide coated glass slide was used as the other electrode. The film of the composite involving poly(β -pinene) and C_{60} was cast on the aluminum electrode and the indium-tin-oxide electrode was placed on it. Pressure was

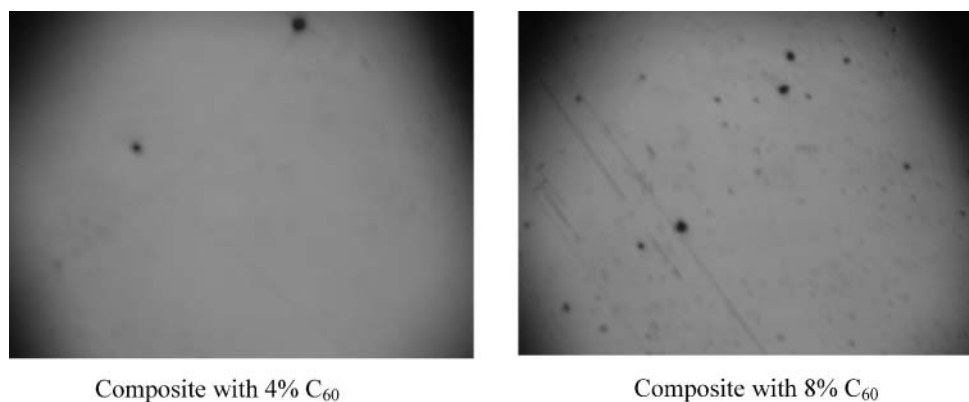


Fig. 2. Optical micrographs (magnification 50x) of the composite films. The composite with 4% by weight of C_{60} is more homogeneous than that with 8% by weight of C_{60} .

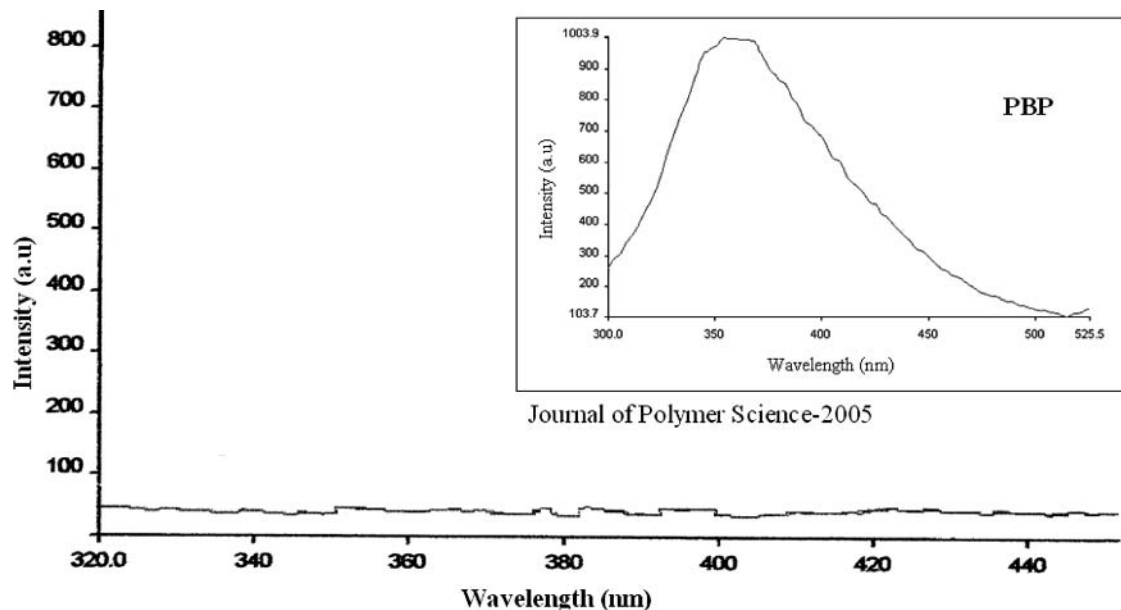


Fig. 4. Quenching of photoluminescence of the composite involving poly(β -pinene) and C_{60} (2% by weight) for excitation at 280 nm. The inset shows the photoluminescence spectrum of poly(β -pinene) by itself for excitation at 280 nm.

applied to keep the composite and the electrodes in contact. The film thickness was about $1 \mu\text{m}$. Films thinner than that were not used in these experiments to avoid short-circuit between the electrodes. Aluminum electrode was connected to the negative terminal of a high impedance electrometer (Keithley 617 Programmable Electrometer) (13-15) and the indium-tin-oxide electrode was connected to the positive end of the electrometer to measure the photovoltage. The indium-tin-oxide electrode was placed face-up to ensure

that the light is incident on the polymer through this electrode. The experimental setup is shown in Figure 5. The inset in the Figure 5 shows the spectrum of the white light source used in these measurements. In addition, a nitrogen laser (325 nm and 425 nm) was used as a light source for these measurements. Besides the composite samples, poly(β -pinene) by itself and C_{60} by itself were also used in the sandwiched structure for photovoltaic measurement as control experiments.

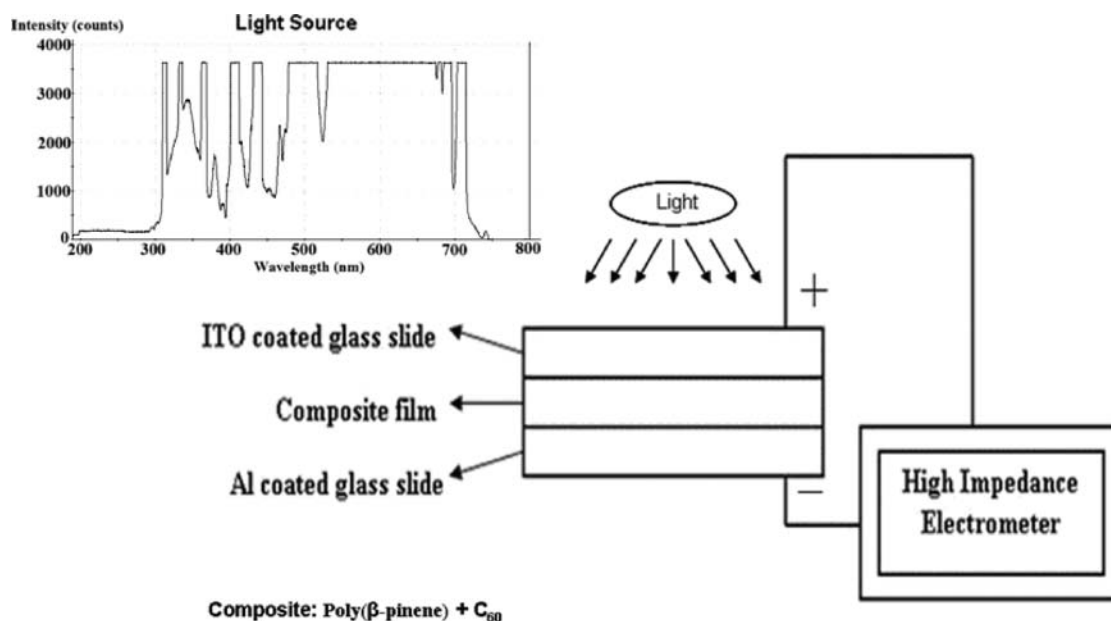


Fig. 5. Experimental setup for measurement of photovoltages.

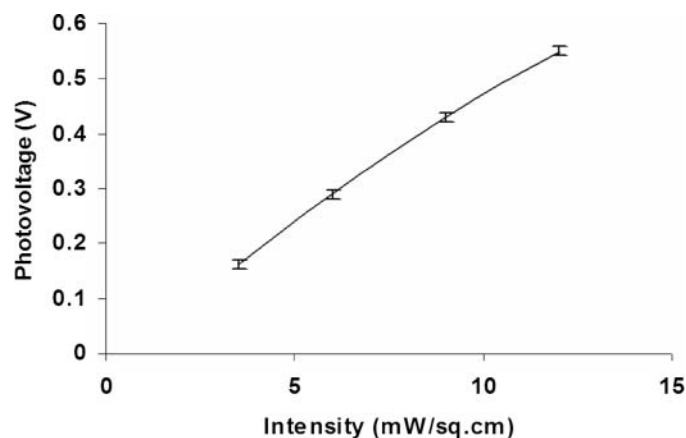


Fig. 6. Photovoltage as a function of incident light intensity for a composite containing 4% C_{60} by weight.

The photovoltage produced for a composite involving poly(β -pinene) and 4% C_{60} by weight was recorded for different intensities of the incident light. White light source with a wavelength range of 300–700 nm was used. It was observed that the photovoltage produced increased with increase in the intensity of the incident light as shown in the Figure 6. A light intensity of $6\text{mW}/\text{cm}^2$ yielded a photovoltage of 280mV. For poly(β -pinene) by itself and C_{60} by itself no appreciable photovoltage was observed. This shows that the measured photovoltage is due to the interaction between poly(β -pinene) and C_{60} .

Photovoltages were recorded for the composites having different concentrations of C_{60} at different intensities of incident light. Table 1 shows the photovoltage produced for composites having different concentrations of C_{60} at different intensities of the incident light. Measurements were also performed for composites having different concentrations of C_{60} using Nitrogen laser operating at 325 nm with a fixed intensity of $2\text{mW}/\text{sq.cm}$. The results are shown in the Table 2. In addition, another line from the nitrogen laser with wavelength of 425 nm was used for such experiments but no measurable photovoltage was observed. This is because pristine poly(β -pinene) does not absorb significantly at 425 nm.

Table 1. Photo-voltages produced for composites with different concentrations of C_{60} at different intensities of light

Intensity Of Incident light (mW/cm^2)	Photo-voltage (mV)			
	Composite with 8% C_{60}	Composite with 6% C_{60}	Composite with 4% C_{60}	Composite with 2% C_{60}
3.5	110	190	162	80
6	200	290	280	130
9	210	380	430	170
12	255	420	550	210

Table 2. Photo-voltages produced for composites with different concentrations of C_{60} using Nitrogen laser as light source (intensity $2\text{mW}/\text{cm}^2$)

Sample	Photo-voltage (mV)
Composite with 2% C_{60}	20
Composite with 4% C_{60}	80
Composite with 6% C_{60}	39
Composite with 8% C_{60}	18

It was observed that the composite involving poly(β -pinene) and 4% C_{60} by weight showed better performance when compared to the composites involving poly(β -pinene) with other concentrations of C_{60} . This is due to the better homogeneity of the composite involving poly(β -pinene) and 4% C_{60} by weight when compared to other composites. For composite films with higher weight percentages of C_{60} , clusters of C_{60} were formed leading to lower interaction with the polymer double bonds. As a result, less photo-induced charge-transfer and smaller photovoltages were observed (Tables 1 and 2). As Figure 6 shows, the photovoltaic device under the present configuration can be used in photo-detector application in the ultraviolet regime. Photovoltaic cells for power generation will need a more refined configuration involving thinner composite films that will allow larger currents for the devices.

In the composite involving poly(β -pinene) and C_{60} , the polymer, poly(β -pinene) acts as an electron donor and the C_{60} acts as an electron acceptor. When light is incident and absorbed by the polymer, electron hole pairs are produced. From this excited state of the polymer, electron is transferred to C_{60} as shown in Figure 7. The electrons are then transported to the aluminum electrode by the C_{60} and

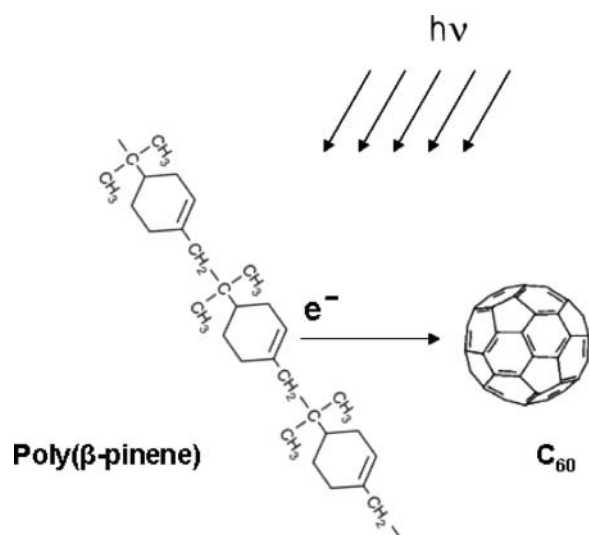


Fig. 7. Schematic of photo-induced electron transfer from poly(β -pinene) to C_{60} .

the holes are transported to indium tin oxide electrode. This transportation of electrons and holes produces the observed photovoltage. The observation that the nitrogen laser at 325 nm produces photovoltage while the same laser at 425 nm does not produce significant photovoltage implies that electron-transfer occurs only from the polymer to C_{60} but not vice-versa. Further studies on efficiency and current ratings of the cells are under progress.

4 Conclusions

Photo-induced charge-transfer and resulting photovoltaic effect in composite films involving a nonconjugated conductive polymer and C_{60} have been observed for the first time. It was observed that the composite 4% C_{60} by weight produced a photovoltage of 280mV for an incident light intensity of 6 mW/sq.cm. The photovoltage produced increases with increase in the intensity of the light. It was also observed that the composite with 4% C_{60} showed better performance when compared to the composites having other concentrations of C_{60} . This photovoltaic cell has many applications at a lower cost in the areas of solar cells, photo-detectors, photo-sensors, etc. While pristine poly(β -pinene) has significant photoluminescence (peak at 360 nm) for excitation at 280 nm, the photoluminescence is quenched when C_{60} is added to poly(β -pinene) to form the composite. This shows that the observed photovoltaic effect is due

to photo-induced charge-transfer from the isolated double-bond of the polymer to C_{60} .

References

1. Sharma, N.S. (2006) *Materials Chemistry and Physics*, 100, 345.
2. Brabec, C.J., Sariciftci, N.S. and Hummelen, J.C. (2001) *Advanced Functional Materials*, 11(1), 15.
3. Spanggaard, H. and Krebs, F.C. (2004) *Solar Energy Materials and Solar Cells*, 83, 125.
4. Kearns D.R. and Calvin M. (1958) *J. Chem. Phys.*, 29, 950.
5. Glenis, S., Horowitz, G., Tourillon, G. and Garnier, F. (1984) *Thin Solid Films*, 111(2), 93.
6. Yamanari, T., Taima, T., Hara, K. and Saito K. (2006) *Journal of Photochemistry and Photobiology A: Chemistry*, 182, 269.
7. Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.E. and Smalley, R.E. (1985) *Nature*, 318 (6042), 162.
8. "Organic Photovoltaics, Mechanisms, Materials and Devices", Sariciftci, N.S., Sun, S.-S., Taylor & Francis, New York, 2005.
9. Morita, S., Zakhidov, A.A. and Yoshino, K. (1992) *Solid State Commun.*, 82(4), 249.
10. Morita, S., Kiyomatsu, S., Yin, X.H., Zakhidov, A.A., Noguchi, T., Ohnishi, T. and Yoshino, K. (1992) *J. Appl. Phys.*, 74(4), 2860.
11. Thakur, M. (1988) *Macromolecules*, 21, 661.
12. Vippra, P., Rajagopalan, H. and Thakur, M. (2005) *Journal of Polymer Science, Part B: Polymer Physics*, 43(24), 3695.
13. Benda, M. (1970) *Phys. Stat. Sol. (a)*, 2(4), K225.
14. Chu, S.Y., Ye, Z. and Uchino, K. (1994) *Smart Mater. Struct.*, 3, 114.
15. Poosanaas, P. and Uchino, K. (1999) *Materials Chemistry and Physics*, 61(1), 36.