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Article

Study of the Kapton-H Fundamental Absorption Edge and Tailing Behaviour

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Abstract

Kapton-H type is an optical plastic with an UV-Vis-NIR spectrum characterized by abrupt absorbance change at a wavelength of ca. 550nm. Such sharp optical discontinuity, known as fundamental absorption edge, has been investigated by the Tauc plot method and a band gap energy (E_g) of (2.22 ± 0.05) eV for an indirect transition model has been found. The Cody plot has been also applied and a similar result was found. The Urbach rule applied to the spectrum tail has provided an Urbach energy value (E_u) of ca. (418 ± 2) meV, which is a quite high value, fully compatible with the highly disordered structure of this sterically rigid amorphous polymer. Cut-on wavelength (550nm), visible transparency (T% of ca. 80), and other relevant optical characteristics of Kapton-H type have been evaluated too.

Keywords: Kapton-H type; UV-Vis spectroscopy; cut-on; band gap energy; Urbach energy; structural disorder

1. Introduction

Kapton-H type is a high performance thermoplastic polymer, well-known for its high thermal stability, great electrical/thermal insulation capability, good resistance to ionizing radiations (e.g., X-rays), etc. [1]. However, Kapton-H is an optical-grade plastic too [2]; indeed, it is a perfectly transparent organic solid [3] with a refractive index value quite close to that of silica glass (ca. 1.70, sodium D-line, 589.0nm). The Kapton-H high optical transparency is due to its amorphous nature, that makes this polymer completely unable to scatter visible light. Kapton-H has two important functional properties that lead it as very attractive material for industrial applications. Firstly, Kapton-H films uniformly absorb the full ultraviolet spectral region [4], that is, the electromagnetic radiations with a wavelength ranging from 190nm to 400nm and therefore it can be used as shield for this type of ionizing radiation (precisely, radiations belonging to the UV-A, -B and -C spectral sub-bands are completely extinguished). Since Kapton-H is a high performance thermoplastic polymer widely used in space technology [5], such an additional shielding characteristic expand further the advantages deriving from its use in this special area of technology (UV radiation is particularly abundant outside the earth atmosphere). In addition, this optical plastic strongly absorbs visible light in the 400-500nm spectral range (i.e., violet, blue and green lights) and such strong optical absorption causes the characteristic bright gold-yellow coloration showed by this plastic material [6], that consequently can be industrially exploited for applications as color filter [7]. In particular, yellow color filters are very useful optical devices since they have a number of industrial applications, varying from the pharmaceutical packaging, to snow/night goggles, safety lighting systems, car headlights and/or fog lights, etc. [8,9].

The photo-excitation of Kapton-H in ultraviolet/visible spectral regions can be accurately described by using the band theory [2]. This solid-state physical theory can be indifferently applied to all type of covalent crystals and amorphous solids included polymers, glasses and other dielectric substances [10–12]. The special absorption behavior of Kapton-H is a consequence of the interband

electronic transitions (i.e., HOMO-LUMO transition and transitions involving energetic levels in the conduction band of higher energy).

Here, the absorption properties of Kapton-H in the UV-Vis-NIR spectral regions have been in-depth investigated by using optical spectroscopy measurements, combined with standard analysis methods like the Tauc plot [13], Urbach rule [14], Cody plot [15], etc. In particular, the performed analyses have allowed to evaluate Kapton-H electronic/optical characteristics like the band gap energy (E_g), Urbach energy (E_u), visible transparency percentage, cut-on wavelength and to quantify the structural disorder in this amorphous material.

2. Materials and Methods

Kapton-H specimens were provided by Wetec (GmbH, Germany) in form of foils. Optical spectra were obtained by using a double beam UV/Visible spectrophotometer (VWR, UV-6300PC Spectrophotometer). These spectra were obtained in the 190-1100nm wavelength range with low scan speed and a scan step (resolution) of 0.5nm (slit 0.0). Spectra have been processed by a devoted analysis software (UV-Vis Analyst, Version 5.44, VWR). In particular, Kapton-H was tested in form of films (rectangular specimens, 1cmx3cm), without to use any type of reference sample. These rectangular films were stuck to the instrument sample holder by paper adhesive tape. Film thickness for absorption coefficient determination was measured by using a digital micrometer and resulted of 38 μ m.

3. Results

Optical spectra of Kapton-H films have been obtained in both absorbance (A) and transmittance (T) modes in the 190nm-1100nm spectral range (see Figure 1a,b). As visible, the optical spectrum is characterized by a very sharp transmittance change in the visible light spectral range (precisely the green-yellow region). In particular, this rapid variation of the visible light transmittance value takes place at a wavelength of ca. 550nm; indeed, the Kapton film transmittance percentage is close to 80 at wavelengths higher than 600nm and close to zero at wavelengths lower than 500nm. Therefore, the transmittance switching can be assumed to take place at a wavelength value of ca. 550nm. It must be pointed out that at wavelengths lower than 500nm the transmittance value assumes a continuous value very close to zero, up to the extreme spectroscopically measurable spectral value (190nm). Since the transmittance change starts at 600nm and complete at 500nm, it is possible to assume for the Kapton-H optical filter a cut-on value located at 550nm.

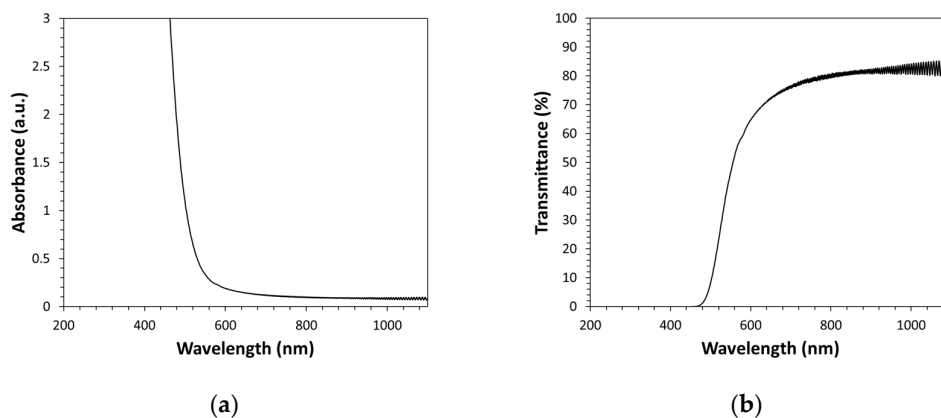


Figure 1. Optical spectra of a Kapton film in the absorbance (a) and transmittance (b) modes.

The absorption coefficient, α , has been calculated from the raw absorbance data by using the Lambert's law, (i.e., $\alpha=A/d$, where d is the path length of light, corresponding to the film thickness $d=0.038$ mm) and the corresponding wavelength values have been converted to energy (expressed in eV) by using the equation: $\lambda(\text{nm})=1239.8/E(\text{eV})$ [14]. A plot of absorption coefficient versus energy in

semi-logarithmic scale has been made (see Figure 2). This type of spectrum representation has been used to estimate the Urbach energy value from the slope of the linear part of the spectrum. Indeed, according to the Urbach rule, the absorption coefficient (α) grows exponentially with the increasing of the photon energy (E):

$$\alpha = \alpha_0 \cdot \exp(E/E_U) \quad (1)$$

which in logarithm form becomes:

$$\ln(\alpha) = \ln(\alpha_0) + (1/E_U) \cdot E \quad (2)$$

The inverse of this slope corresponds precisely to the Urbach Energy of Kapton expressed in eV and this quantity is directly proportional to the structural disorder in this amorphous polymer. A value of (418 ± 2) meV has been found and such quite high energy indicates a high disordered structure of this amorphous polymer, probably due to its steric rigidity.

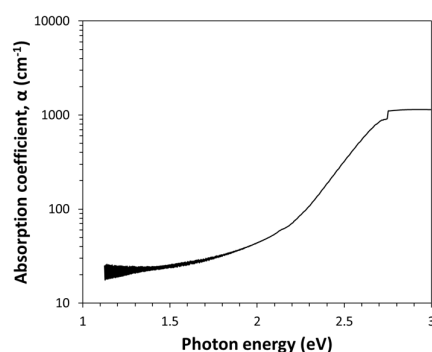


Figure 2. Plot of the absorption coefficient vs. photon energy in semi-logarithmic scale.

The band gap energy (E_g) value is a further important physical property of Kapton-H, that can be optically estimated. The measurement of the band gap energy is really essential in both the semiconductor and nanomaterial industries, however it can be very useful also in the case of dielectric substances like polymers and glasses since this quantity defines the electrical and thermal insulation capability of the material. This quantity can be evaluated by drawing the Tauc plot for a direct and indirect transition model, with the aim to establish which model provides a better fitting of the experimental optical data. According to the Tauc plots shown in Figure 3a,b, data were more conveniently described by an indirect band gap transition model (i.e., $(\alpha h\nu)^{1/2} = k(h\nu - E_g)$), which is the classical expression used by Tauc for the amorphous semiconductors. Such indirect transition model has provided an E_g value of (2.22 ± 0.05) eV (intercept of the linear part of the graph), which is in accordance with the value given in the literature for this type of amorphous polymer [2]. The optical measurement of the band gap energy value can be useful also for analytical uses, that is the identification of polymers of unknown nature by comparing their E_g values with values given in the literature for different polymers.

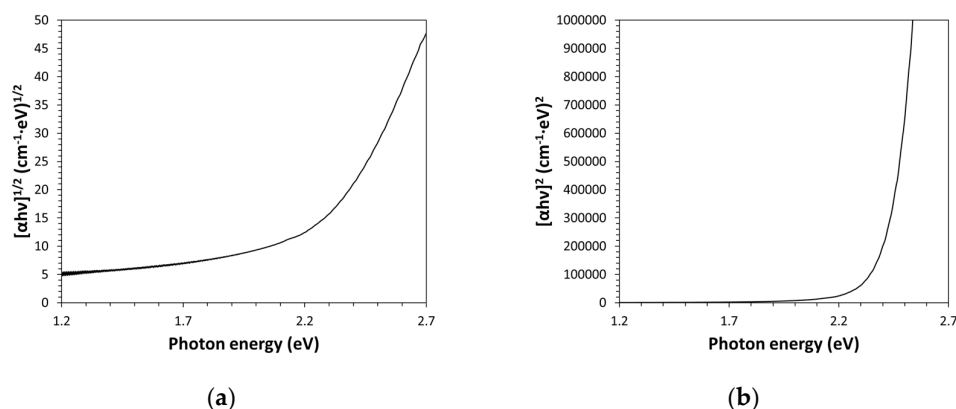


Figure 3. Tauc plot for direct (a) and indirect (b) semiconductor models.

Alternatively, the band gap energy of Kapton-H can be determined by elaborating the optical absorption measurements according to Cody plot method. The Cody model is based on a constant dipole matrix approximation and it is related to the absorption coefficient by the following expression: i.e., $(\alpha/h\nu)^2 = k(h\nu - E_g)$. As shown in Figure 4, this plot shows a linear behavior in the high photon energy range. Such an approach has provided a value of E_g of (1.82 ± 0.05) eV, which is slightly lower than that estimated by the Tauc plot for the indirect transition model and therefore slightly different from the value usually assigned this polymer [2].

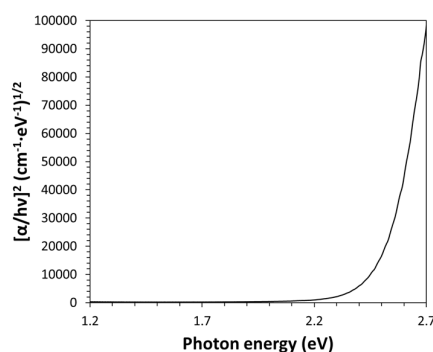


Figure 4. Cody plot for the Kapton-H type.

Finally, the Kapton-H optical spectrum has a quite standard behavior, that includes a dramatic transmittance change from a very high value (ca. 80%) to zero at the cut-on wavelength. Compared to the typical solid polymer spectral behavior, Kapton-H has the following two peculiarities: (i) the cut-on is located just in the middle of the visible spectral range, i.e., at ca. 550nm, while such transition is typically observed in the UV-A/B region for other types of polymer and (ii) a pronounced exponential decay (i.e., the so called Urbach tailing) is visible in the region of the fundamental absorption edge. Owing to the quite sterically rigid structure, short-range order in this amorphous polymer should be much lower than in polymers with a flexible backbone.

4. Discussion

The optical investigation of the Kapton-H electronic structure is useful for different reasons. For example, this investigation may allow (i) to establish which technological potentialities has such type of polymer in technological fields like optics (e.g., color filters, UV-blocking optical windows, etc.); (ii) to identify an unknown polymer sample based on its characteristic band gap energy value; (iii) to acquire in-depth structural information on it (e.g., structural disorder content); etc. The electronic structure of a polymer can be determined by investigating its capability to interact with photons of

different wavelengths. In particular, absorption measurements in different light spectral regions are required in order to obtain information on the full electronic structure of the polymer. Here, the optical spectrophotometer has allowed to measure the Kapton capability to absorb photons of low energy (near infrared radiation, NIR), medium energy (visible radiation) and high-energy (ultraviolet radiation, belonging to the A, B and C sub-bands). Such photon absorption is a direct consequence of the electronic transitions that can occur in the solid phase and therefore, in turn, the absorption measurement allows deducting the external (valence) electronic configuration of the polymer. According to the achieved optical spectra, Kapton like other solid polymers have a band electronic structure, that is, contains wide spatial regions made of energetically very close levels (delocalized orbitals) that can be both filled or unfilled by electrons (valence and conduction bands, respectively). The measurement of absorbed photon energy has allowed to establish both spacing and extension of these bands (i.e., band edge energy corresponding to the HOMO-LUMO transition).

It must be pointed out that optical spectroscopy practically constitutes a universal characterization technique for polymers; indeed, optical spectra can be obtained for both amorphous and semi-crystalline polymers by using adequately thin films. As a consequence, the optical measurement of the band gap energy value can be used as a simple analytical approach to establish the nature of an unknown polymeric sample; indeed, each polymer has a own specific value of E_g .

On the other hand, the Kapton optical absorption for energies below the fundamental optical absorption edge (Urbach region) is exponential in nature and this behavior can be in-depth investigated and the curvature can be quantitatively described by the Urbach energy value, which reflects the amount of local intermediate states and therefore the level of structural disorder characterizing the polymeric system. Such information coming from this simple optical analysis of the amorphous polymer electronic structure makes possible to classify amorphous polymers based on their disorder content. Finally, in the case of Kapton-H, this investigation has evidenced a high disorder content, which is compatible with the amorphous nature of a stereorigid polymer.

5. Conclusions

The Kapton optical characterization in the spectral region of the fundamental absorption edge has shown: (i) strong optical absorption for photons with energy larger than $(2.22 \pm 0.05) \text{ eV}$ (band gap energy values obtained by the Tauc and Cody plots); (ii) indirect band gap behavior (the best Tauc plot fitting has been obtained with the indirect transition model, which is a characteristic of all amorphous semiconductors); (iii) 80% transmittance for photons with energy values below $(2.22 \pm 0.05) \text{ eV}$; and (iv) significant tailing ($E_u = (418 \pm 2) \text{ meV}$), as expected for a high disordered amorphous polymer. This special optical behavior allows Kapton-H to be used for fabricating yellow color filters, UV-absorbers, thermally-resistant optical windows, etc.

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