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Journal of Engineering and Technology Research

Full Length Research Paper

# Analysis of differences in internet user experiences and virtual network activities in Taiwan

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Considered a crucial industrial development in the 21st century, the Internet has had a marked effect in shaping modern society. The ongoing development of handheld mobile Internet devices has enabled services in the virtual world to be updated constantly, thereby providing numerous options regarding the virtual network interactions and activities of Internet users. Among the various virtual network activities, people and organizations can form friendships, purchase commercial goods, engage in virtual role-playing activities, and form virtual communities or families through the digital devices. For this study, we adopted an array of statistical methods, including descriptive statistics, independent samples *t* tests, analysis of variance, and factor analysis, to explore the differences in how virtual network behavior factors influence users from varying backgrounds and with varying levels of experience using the Internet. The analysis results revealed the effects of the time spent online per day, the length of time spent using the Internet, and owning multiple network accounts.

Key words: Virtual network world, online network activity, user behavior, virtual community.

#### INTRODUCTION

Considered a crucial industrial development in the 21st century, the Internet has had a marked effect in shaping modern society. The ongoing development of handheld mobile Internet devices has enabled services in the virtual world to be updated constantly, thereby providing numerous options regarding the network interactions and activities of Internet users (Jung and Kang, 2010; Mantymaki and Salo, 2011; Lin et al., 2011). Among the various network activities, people and organizations can form friendships, purchase commercial goods, engage in virtual role-playing activities, and form virtual communities or virtual families using Internet devices (Eisenbeiss et al., 2012).

Subsequently, ties and communication between people in the virtual world have been extended to the real world, and the boundary between the two worlds has become blurred. Internet romances and online fraud demonstrate that trust exists in online interpersonal relationships, which is a key factor that influences people's willingness to communicate and share information (Gefen, 1997; Jarvenpaa et al., 1998). In virtual communities, familiarity with community members and perceived trust have a positive effect on people's knowledge-sharing intentions (Zhao et al., 2012). A widely reported problem among

\*Corresponding author. E-mail: tsungyi@mail.nhu.edu.tw Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> <u>License 4.0 International License</u> network users is that they do not trust the security of Web sites, and concerns have been voiced regarding Web site security mechanisms. Because of the minimal entry requirements, access to Web sites is difficult to control, and online criminal activities are frequently reported. Numerous issues regarding personal privacy infringements resulting from using the Internet have emphasized the importance of privacy security and protection (Yang, 2011). The disparity of interpersonal social interactions between virtual and real-world network activities, however, raises unprecedented problems. Consequently, given the deficiencies of current legal systems, protecting people's rights and interests online remains difficult (Yang, 2011).

Results of online surveys have revealed that the more prevalent the Internet becomes and the larger its application scope, the more people rely on it in their daily lives. Most real-world activities correspond to similar activities on the Internet, such as forming friendships, sharing information, learning new skills, trading or purchasing goods, and playing online games or engaging in other recreational activities (Mantymaki and Salo, 2011).

This study investigated the phenomena of network activities in the daily lives of network users and the possible factors influencing online use behavior and decision-making at the individual level. Previous studies have primarily focused on a single dimension, such as privacy, rather than adopting a holistic perspective. Therefore, this study adopted a more comprehensive method and simultaneously investigated six dimensions and their possible interacting influences. Adopting the perspective of users, we gathered and analyzed data regarding the network behaviors of network users in Taiwan. In this paper, we discuss the factors that influence such behavior and provide suggestions for practitioners and researchers. For this study, we adopted an array of statistical methods, including descriptive statistics, independent samples t tests, analysis of variance (ANOVA), and factor analysis, to examine the factors that influence the quality of user behavior for network activity and other relevant variables, from which 31 questionnaire items were derived. After conducting a questionnaire survey, data were organized, analyzed, and summarized through an analytical process that involved (1) collecting information on the respondents' background and their Web experiences to use as the basis for the statistical analysis; (2) examining the various backgrounds of users to determine the influence of network behavior factors; and (3) exploring the differences among user experiences to determine the influence of network behavior factors. We explored the factors influencing the guality of users' network behaviors by examining their current status and behavioral patterns to provide a reference for future researchers or network operators seeking to enhance the quality of their network services.

#### LITERATURE REVIEW

Depending on their purpose, network activities can be classified as related to virtual communities, online electronic trading, online friend-making, digital leisure and recreation, and e-learning (Yoo, 1996; Jung and Kang, 2010). Each type of network activities involves a unique pattern of management and operation. Virtual communities are a form of online virtual interpersonal relationships, where members share their experiences, information, and knowledge (Rheingold, 1993; Jung and Kang, 2010; Zhao et al., 2012). Examples of virtual communities include forums, blogs, Wikis, and bulletin board systems (BBS), through which users with similar sentiments or interests but distinct backgrounds establish virtual social networks by communicating and interacting through these networks (Lu et al., 2010). A virtual community is a virtual organization comprising members who might not know each other (Kannan, 1998; Lee et al., 2002). Currently, opinions from online communities can influence consumer purchase decisions (Zhao et al., 2012). Underlying user intentions to participate in virtual social networks are five key values: purposive value, selfdiscovery, entertainment value, social enhancement, and maintaining interpersonal connectivity (Cheung et al., 2011). Currently, the most popular social networks or community Web sites in Taiwan are (in order of popularity) Facebook (used by approximately 80% of Internet users in Taiwan), Wretch, Yahoo, Plurk, and Atlaspost. Facebook is the most widely adopted and popular social networking Web site among students worldwide (Cheung et al., 2011). In this study, the most frequently reported user behaviors in virtual communities are summarized as follows: (1) registering for membership to a specific social community; (2) providing false information to win the trust of other users; (3) obtaining personal information through cheating or fraud; (4) reading or sharing information; (5) discussing popular topics; (6) participating in real-world activities that are extended from virtual communities; (7) expressing personal opinions (e.g., clicking a "like" button); and (8) massive researching by using Internet media, such as blogs and forums (e.g., the "human flesh search engine").

Online trading benefits both enterprises and users, and it meets individual demands for trading or purchasing services. Using networks and mobile devices to conduct trading, online trading or purchase behaviors are relatively free of temporal and spatial constraints (Woo et al., 2004; Lin et al., 2011). User behaviors related to Internet transactions or trade can be summarized as follows: (1) after completing a registration procedure where a user's identity has been authenticated, the user may initiate an Internet transaction or open an online store; (2) sharing purchase experiences; (3) launching promotional campaigns to increase brand exposure; (4) searching for product information through online word-ofmouth (WOM); (5) comparing prices; (5) managing cash flow and logistics after selling or purchasing an item; (6) making mutual evaluations after purchasing goods or services; and (7) bidding in an online auction.

For people who exhibit antisocial tendencies in the real world and experience difficulty forming friendships, online social activities may complement and mediate their interpersonal problems because they can initiate conversations with strangers about their feelings, thoughts, perceptions, and values rapidly without fear of rejection (Young, 1997). An exceptionally high percentage of users establish new friendships and interact and chat with other users through the Internet (Eisenbeiss et al., 2012). Two schools of thought exist regarding online or virtual friend-making; the first one holds that the Internet offers and can create new types of interpersonal relationships (Rheingold, 1993), and the other perspective contends that using the Internet undermines and leads to the loss of traditional interpersonal relationships (Beninger, 1987). In recent years, the development of social network-based electronic commerce has become a new business trend (Lu et al., 2010). In this study, Internet users' online friend-making behaviors are summarized as follows: (1) registering for membership under a pseudonym; (2) interacting with online friends in a virtual space; (3) fulfilling real-world fantasies through role-playing activities involving virtual characters; (4) engaging in real-world interactions as an extension of virtual interactions; and (5) updating personal statuses and forwarding messages.

#### **RESEARCH METHODOLOGY AND DEFINITIONS**

According to the objective of this study, all Internet users were considered suitable for participation as a research target or questionnaire respondent, regardless of the type of device they use to connect to the Internet. We administered a questionnaire as a tool for acquiring research data. Considering the geographical restrictions, in this study, we adopted a convenience sampling method to collect data. Statistical analysis tools were used during the analytic phase, and the research data underwent a descriptive statistical analysis. For statistically significant differences in the data, Scheffé's method was applied for a post hoc comparison to examine the variance between the groups of network users.

In addition to having various reasons and motivations for using the Internet, network users may exhibit distinct thinking patterns that are based on how they perceive and respond to external stimuli. Previous studies have shown that user types can be differentiated based on various perspectives. For example, from the perspective of information needs, users may have different preferences and information behaviors (Wilson, 2000). Regarding personality traits, individual behaviors are consistent and regular because each person possesses source traits. According to Cattell (1972), each person's unique personality comprises 16 personality factors. Depending on how often they use networks, users can be categorized as digital leaders, connoisseurs, hippies, and onlookers. However, various sources of stimulation in the real and virtual world as well as individual motivations have distinct influences on the network behaviors of users. Factors influencing user network behaviors and decision making comprise the six dimensions of trust, reputation, network security, WOM, network privacy, and Web ease-of-use. This study adopted these

dimensions to form the theoretical basis of the questionnaire design. This study adopted 31 questions based on these six dimensions, which are defined as follows:

(1) Trust: The dimension of trust refers to a positive expectation that the other party will honor a verbal promise (Deutsch, 1973; Boon and Holmes, 1991). A trust relationship is the foundation on which people choose partners for cooperation and mutual belief (Fuhrt, 2005). Numerous studies have shown that user trust in a Web site exerts a positive influence on user purchase intentions (Lim et al., 2006; Wulf et al., 2001; Jarvenpaa and Tractinsky, 1999; Lin et al., 2011). Based on our review of relevant literature (Mayer et al., 1995; Krackhard & Brass, 1994), the questions for the trust dimension are (Q1) "In the real world, I tend to believe others except under special circumstances or for certain reasons"; (Q2) "I believe the opinions and comments of online friends who I have never met in person"; (Q3) "Information from the Web can and should be trusted"; (Q4) "Evaluative comments found online can be trusted"; (Q5) "Internet advertisements can be trusted"; (Q6) "When I browse or log onto certain Web sites, it means I support and identify with these Web sites"; (Q7) "When a stranger adds me as a friend, I add him or her to my contact list or as a friend."

(2) Reputation: This dimension refers to the credibility or fame that a person or corporation utilizes for social activities, or the influence of a corporation's brand image (Sharif and Kalafatis, 2005). Numerous previous studies have shown that a positive reputation is a key factor for building or creating trust (Antony et al., 2006; Boot and Greedbaum, 1993; Moukas et al., 1999; Resnick and Zeckhauser, 2000; Jarvenpaa et al., 1999; Kim et al., 2008). Currently, indicators for measuring the brand image of a company include company image, WOM reviews, popularity, and company reputation. By adopting the opinions of various scholars (Dowling, 1994), we developed the questions to measure the reputation dimension: (Q8) "I search for product information regarding wellknown Internet brands"; (Q9) "When making decisions, I refer to online evaluations first or as a priority"; (Q10) "A company Web site benefits the company's image"; and (Q11) "Reputation is a decisive indicator that influences my participation or performance in network activities.'

(3) Network Security: Network security presents a challenge for network activities. Considering the rising annual trend in cyber or online crime, if a business can guarantee or commit to providing a secure network for customers, it would considerably reduce the cost of mutual monitoring and enhance user trust when making purchases. Questions for the network security dimension in this study are: (Q12) "I think existing laws are sufficient to protect my rights and interests on the Internet"; (Q13) "There are adequate security and protection facilities on the Internet"; (Q14) "The Internet is a stable and secure virtual environment"; and (Q15) "I update my passwords and antivirus software regularly."

(4) Word-Of-Mouth (WOM): When users engage in network activities, their decision-making is subject to information obtained from other users, and they share information or comments with other users. Facilitated by the network platform, the transmission of WOM can exert a widespread influence on the purchase intentions of other users. The influence of a social network includes both positive and negative WOM (Kuan and Bock, 2007). WOM has been considered as a crucial factor for businesses and brands competing with each other (Murray, 1991; Bone, 1995). After summarizing the findings of previous studies (Kim and Prabhakar, 2004; Kuan & Bock, 2007), we designed the following questions regarding the WOM dimension: (Q16) "I am willing to share my experiences of using the Web with others"; (Q17) "The positive or negative WOM of online users affect my willingness to participate in network activities"; (Q18) "I deliberately spread positive or negative WOM related to Web sites"; (Q19) "I am particularly concerned with opinions provided by opinion leaders on the Web"; and (Q20) "I think Web sites with higher popularity have more positive WOM".

Dimension	Question no.	Cronbach's α	$\alpha$ for the overall questionnaire
Trust	1, 2, 3, 4, 5, 6, 7	0.668	
Reputation	8, 9, 10, 11	0.625	
Security	12, 13, 14, 15	0.857	0.947
WOM	16, 17, 18, 19, 20	0.758	0.847
Privacy	21, 22, 23, 24, 25, 26	0.685	
Web ease-of-use	27, 28, 29, 30, 31	0.795	

Table 1. Results of reliability and validity analysis.

(5) Network Privacy: When users engage in network activities, their private information should be protected from infringement. Wellestablished content or information and privacy protection is a key factor attracting online users to participate in Internet communities (Chang et al., 1999). Effective consumer privacy protection in ecommerce is a crucial condition for developing e-markets (Yang, 2011). When Facebook allowed greater access to the personal information of its users, there was an increase in information abuse, identity theft, and other privacy risks (Whelan, 2005). Based on the opinions of experts (Malhotra et al., 2004), we developed the following questions for the network privacy dimension: (Q21) "When participating in network activities, I feel that my privacy could be violated at any time"; (Q22) "The more rigorous the Internet privacy protection policies are, the more secure the Internet is and the more guarantees it provides"; (Q23) "I believe the privacy assurance statement provided by Web sites"; (Q24) "I participate in network activities anonymously or by using a pseudonym"; (Q25) "I do not care about my personal information being disclosed on the Internet"; and (Q26) "I am excited when someone searches for my personal information."

(6) Web Ease-of-use: This dimension refers to the convenience and ease of understanding how various network activity interfaces are operated. Perceived ease-of-use and perceived usefulness are critical variables that influence the attitudes and behaviors of information system users (Davis et al., 1989). Unfamiliarity with a Web site is likely to cause users to visit other sites. By referencing and summarizing the opinions of experts (Yoo, 1996; Davis et al., 1989), we designed questions for the ease-of-use dimension, including (Q27) "It is easy to participate in virtual community activities"; (Q28) "Online shopping is easy"; (Q29) "Making friends online is easy"; (Q30) "Online recreational or leisure activities are easy to perform"; and (Q31) "Learning ina digital environment is easy."

#### BEHAVIORAL DIFFERENCE ANALYSIS

#### **Data collection**

Before issuing the formal questionnaire, a pretest was conducted to evaluate the appropriateness of the questionnaire semantics and content. Nonsignificant questions were removed according to the results of an analytical evaluation of the pretest questionnaire. For the final questionnaire, we revised the wording of the questions to fit the context of this study. We administered 50 pretest questionnaires and received 42 responses, among which 39 were valid. Using the valid questionnaires, we analyzed the response to determine the reliability of the questionnaire items. The results

showed that (1) The correlation coefficients of the 31 questions and factor loadings all exceeded the standard of 0.3, except for Q2, which was eliminated; and (2) A KMO measure of sampling accuracy test and a Bartlett test of sphericity yielded a KMO value of 0.867 and a Bartlett test of sphericity value of 3022.658 (p < 0.001). The factor analysis results indicated that two pairs of variables, reputation and WOM as well as network security and privacy, had similar attributes. For this study, we used Cronbach's  $\alpha$  coefficient to analyze the internal consistency of the questionnaire items in terms of the research dimensions and to assess the reliability and validity of the entire questionnaire. A high  $\alpha$ -coefficient represents high consistency among the questions, and indicates that questionnaire items accurately reflect the actual characteristics of the participants. The analysis results in Table 1 show that the Cronbach's α-coefficients ranged from 0.625 to 0.857, and the Cronbach's acoefficient of the overall questionnaire was 0.847, indicating that both the overall questionnaire and each dimension achieved high internal consistency and adequate reliability.

#### Data analysis for samples

For this study, we distributed 310 questionnaires, 293 of which were returned, yielding a response rate of 94.5%. Among the returned responses, 274 of them were valid, yielding the available rate of 88.39%. The demographic variables in this study were gender, age, education level, monthly income, and area of residence (Table 2). Most of the respondents were women (n = 144, 52.6%). Regarding age distribution, most of the respondents were young (that is, 26 to 35 years of age, n = 90, 32.8%) or middle-aged (that is, 36 to 45 years of age, n = 75, 27.4%). The education level of the respondents was concentrated at universities and colleges (n = 151, n = 151)55.1%), followed by senior high school or vocational high school (n = 74, 27%), then junior high school (n = 31, 1)11.3%), graduate school and above (n = 14, 5.1%), and elementary school or below (n = 4, 1.4%). The average monthly income of most respondents was within the NT\$20,001 to NT\$50,000 range (n = 149, 54.4%), followed by NT\$20,000 and below (n = 64, 23.4%). Most

Variable	ltem	Count	Percent
Condon	Man	130	47.4
Gender	Woman	144	52.6
		00	40.0
	15 years or below	28	10.2
	16-18 years	7	2.6
	19-25 years	50	18.2
Age	26-35 years	90	32.8
	36-45 years	75	27.4
	46-55 years	19	6.9
	56 years or above	5	1.8
	Elementary school or below	4	1.5
	Junior high school	31	11.3
Education level	High school	74	27.0
	Four-year or two-year college	151	55.1
	Graduate school or above	14	5.1
	NT\$20,000 or below	64	23.4
	NT\$20,001-50,000	149	54 4
Monthly income	NT\$50,001-80,000	52	19.0
	NT\$80,001-100,000	6	2.2
	NT\$100,001 or above	3	1.1
	Northern Taiwan	127	46.4
	Central Taiwan	127	40.4
	Southern Taiwan	27	40.1
Area of residence	Eastorn Taiwan	Z 1 A	9.9 1 5
	Coffehere island	4	1.0
		5	1.8
	Others	1	.4

Table 2. Sample demographics (n=274).

respondents lived in Northern Taiwan (n = 127, 46.4%) and the Central Taiwan (n = 110, 40.1%).

A cross-analysis of the time spent online per day and gender revealed that most respondents (40.9%) spent less than 2 h/day online. Regarding gender differences, more men (27%) than women (9%) reported used the Internet for a long period each day (that is, > 6 h/day). A cross-analysis of Internet experience and education level showed that most respondents had used the Internet for longer than 5 years (70.8%). Moreover, the results indicated that people have a high level of reliance on the Internet. Including the respondents' education level revealed that higher education levels were associated with greater experience in using the Internet. A crossanalysis of gender and the devices used to connect to the Internet revealed that most respondents used a desktop computer to access the Internet (81%), followed by laptop computers (51.1%). However, with the emergence of mobile networking technologies, almost half of the respondents reported using a smart phone to browse or

connect to the Internet (44.9%). Among these respondents, more women (48%) than men (41%) reported using a smart phone to access the Internet. Regarding the types of network activity that the respondents performed or participated in, most users reported engaging in online community-based activities (62.8%), followed by information searching (58%). Among the virtual community activities, network communities and blogs were the most frequently accessed and employed services. An analysis of online trading activities revealed that women exhibited stronger preferences for online Therefore, in the future, promotional shoppina. campaigns or activities for mobile devices or smart phone applications should be designed to target women's needs in order to create superior effects. Regarding online friend-making activities, instant messaging was the tool most frequently used by interviewees. However, men exhibited a greater preference for playing online games.

Another cross-analysis was performed to determine whether the network activities correlated with user

occupation. The results show that people employed in network-related industries were heavy Internet users (with a low correlation, 25.2%). Currently in Taiwan, the most popular Web sites are Yahoo! (97.8%) for online electronic trading; Facebook (71.5%) for participating in virtual communities; MSN (43.1%) for forming new online friendships; and YouTube (51.1%) for digital leisure and recreation activities. A cross-analysis of gender and whether network activities were performed anonymously showed that most users had one or two anonymous accounts (60.9%), and nearly a quarter of all users owned three to four accounts (23.7%). Comparatively, men typically had more anonymous accounts. More than half of the respondents used different accounts for specific network activities accounted (57.7%). Users older than 46 years of age typically did not use multiple online accounts.

#### Difference for varying background variables

Here presents the results of an independent samples *t* test and one-way ANOVA to explain how the background variables influence network user behavior. When significant differences were identified, Scheffé's method was applied for post hoc multiple comparisons. The users' background variables (gender, age, education level, monthly income, and area of residence) were used as a basis for identifying which factors affected their network behaviors in terms of the six dimensions of trust, reputation, security, WOM, privacy, and Web ease-of-use. The analysis results are detailed as follows:

(1) Gender: Regarding gender, Table 3 shows that among the factors affecting network user behavior, the only factors yielding significant differences between genders were reputation ( $t = -1.262^*$ ) and privacy ( $t = 3.142^*$ ). Possible reasons for these differences include the following: (a) compared to the male respondents, who had their own opinions and were less biased based regarding famous brands and images, the female respondents cared more about brands; (b) a digital divide persists between genders; specifically, men possess broader, deeper, and more values for information knowledge than do women. Consequently, men were more concerned than women regarding privacy-related rights and interests.

(2) Age: Regarding age differences show significant differences in trust ( $F = 3.632^{**}$ ), reputation ( $F = 4.563^{***}$ ), WOM ( $F = 2.629^{*}$ ), and Web ease-of-use ( $F = 3.118^{**}$ ) among the factors affecting network users. Further analyses revealed that all variable pairs for trust, reputation, and Web ease-of-use reached the level of significance, except for WOM. Overall, users younger 15 years of age exhibited a low ratio regarding various factors, indicating that younger user did not possess significant demands for the various influencing factors.

This may be because younger users have been using online networks from an early age; hence, they are less sensitive to being influenced by network behavior factors, and they exhibit lower levels of awareness and precautionary consciousness. This may also explain why social problems generated through the Internet manifest regularly among adolescents. Based on these results, we recommend enhancing efforts to promote Internet safety and educate young people about the involved dangers.

(3) Education level: Regarding the differences in education trust  $(F = 4.659^{**}),$ level. reputation  $(F = 5.243^{***})$ , and Web ease-of-use  $(F = 6.778^{***})$ showed significant differences for influencing network users. Further analyses revealed that the differences between all groups were statistically significant. Overall, higher levels of academic achievement correlated with higher requirements of trust, reputation, and Web easeof-use. Furthermore, the users with higher educational levels were more experienced in networking and using the Internet. Consequently, they possessed a stronger sense of subjective awareness, had more insightful perceptions and ideas for differentiating the influence of external assessments, and they could understand and control information effectively. When reputation and trust levels were high, they did not need to pay special attention or be careful when using the Internet. Thus, trust and reputation enhance Web ease-of-use.

(4) Monthly income: Among the monthly income groups, reputation ( $F = 5.470^{***}$ ), WOM ( $F = 2.632^*$ ), and Web ease-of-use ( $F = 2.688^*$ ) presented significant differences for influencing the behavior of network users. Further analyses revealed that the results for only reputation and WOM achieved statistical significance, whereas Web ease-of-use did not. Generally, the respondents with monthly incomes of NT\$50,000 to NT\$80,000 paid more attention to reputation and WOM, possibly because they are middle-class workers who are excessively rely on external sources of information when making decisions; hence, they rely on the opinions or comments of experts or opinion leaders.

(5) Area of residence: Network security ( $F = 2.889^*$ ), WOM ( $F = 3.905^{**}$ ), and privacy ( $F = 2.787^{*}$ ) exhibited significant differences among respondents living in different areas. Further analyses revealed that network security and privacy groups did not reach the level of statistical significance. WOM was the only factor affecting network users based on their area of residence, where a greater influence was observed for respondents residing in Northern Taiwan compared to those in Central and Southern Taiwan. This is most likely because the lifestyle in Central and Southern Taiwan is more relaxed and not as busy as that in the north of Taiwan. People who rely heavily on the Internet for all matters use online WOM to gather information, and they consider this to be an ideal life tool. The findings in this section indicate that levels of Internet usage in Taiwan differ significantly among areas of residence with different levels of urbanization.

Factor	Gender	Count	Mean	Standard deviation	<i>t</i> -value
Truct	Male	130	3.0013	0.64550	1 010
Trust	Female	144	2.9132	0.55082	1.218
Reputation	Male	130	3.4865	0.59170	-1 262*
Reputation	Female	144	3.5712	0.51009	-1.202
Security	Male	130	3.1769	0.71015	2 016
Security	Female	144	2.9201	0.74365	2.910
	Male	130	3.2154	0.60161	0.269
VVOIVI	Female	144	3.1958	0.60278	0.200
Brivoov	Male	130	3.2590	0.53839	2 1/0*
Flivacy	Female	144	3.0706	0.44319	5.142
Web ease-of-	Male	130	3.6600	0.64731	0.560
use	Female	144	3.7028	0.61587	-0.500
Overall	Male	130	3.2999	0.46981	1 3/2
Overall	Female	144	3.2290	0.40461	1.342

Table 3. Difference analysis of gender and network behavior factors.

\**p*<0.05, \*\* *p* <0.01, \*\*\* *p* <0.001.

## Differences in Internet use experience and network behaviors

Here, the results of a *t* test and one-way ANOVA are detailed to explore the differences in the influence of network behavior factors among network users with varying levels of Internet experience. Regarding the network experience variable, three aspects were examined in this study: time spent online per day and use of multiple online accounts. Factors influencing network users' behaviors were examined based on the six dimensions of trust, reputation, security, WOM, privacy, and Web ease-of-use. The analysis results are detailed as follows:

(1) Time spent online per day: Numerous factors exhibited significant differences for influencing the behavior of network users according to the duration they spent online per day: trust ( $F = 7.654^{***}$ ), reputation ( $F = 4.847^{**}$ ), network security ( $F = 3.052^{*}$ ), WOM ( $F = 3.867^{*}$ ), privacy ( $F = 2.915^{*}$ ), and Web ease-of-use ( $F = 2.750^{*}$ ). Further analyses revealed that excluding Web ease-of-use, all other groups differed significantly, particularly the users who spent more than 6 h/day using

the Internet. These results indicate that the more time a user spends online, the more trust, reputation, network security, WOM, and privacy they demand. Possible reasons for these significant differences may be that (a) users' long-term reliance on the Internet has made them accustomed to network behavior patterns, to the point where there is no boundary between virtual and real worlds; hence, their trust in the Internet has been established; (b) users search for reputation information and evaluative comments on the Internet to compensate for their sense of uncertainty; (c) users place additional emphasis on network security because when using the Internet, the authenticity of online information is difficult to determine, and fraud and cheating occur frequently; (d) users observe and measure online WOM and transmission situations regularly; thus, they are influenced more by online WOM; and (e) compared to general users, experienced Internet users are less concerned about their privacy being breached or infringed upon.

(2) Users with multiple network accounts: No significant differences were observed in the factors influencing network user behavior regarding the use of multiple network accounts. Thus, network users use Internet

services according to their preferences and habits, and the number of network accounts they own does not cause differences in behavior.

#### DISCUSSION

By employing descriptive statistics, t tests, one-way ANOVA, and factor analysis, we explored the various factors affecting user behavior during various network activities in the context of network users in Taiwan. Most studies related to network user behavior have focused on the influence of individual factors. By contrast, this study adopted a holistic factor analysis to investigate the correlations among various factors. We classified network behaviors based on the six dimensions of namely trust, reputation, security, WOM, privacy, and Web ease-of-use. Subsequently, among these influential factors, was conducted and it was discovered that reputation and WOM were of the same type and that network security included privacy. Therefore, the factors influencing online user's behavior could be reduced to four items, that is, trust, reputation, security, and Web ease-of-use. The results of this study may provide suitable decision-making criteria for enterprises when designing marketing plans and promotions in online environments, and they provide criteria for researchers conducting further study in this field.

#### Conclusion

Considering the geographical restrictions, in this study, we adopted a convenience sampling method to collect data because random sampling was not possible. However, the convenience sampling method does not guarantee that all samples possess an equal likelihood of being selected for participation; whether a certain portion of the population or a specific group was excluded remains unknown. Therefore, we recommend that future studies use a larger sample to improve the precision and representativeness of the results. All factors influencing user behaviors in this study were measured using positive indicators. Negative factors, such as risks, cyberbullying, or Internet indulgence, should be included in future studies to assess the effects of both the positive and negative factors on user behavior to enhance the comprehensiveness of current research in this field.

#### **Conflict of Interest**

The authors have not declared any conflict of interest.

#### ACKNOWLEDGMENT

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#### REFERENCES

- Antony S, Lin Z, Xu B (2006). Determinants of escrow service adoption in consumer-to-consumer online auction market: an experimental study, Decis. Support Syst. 42(3):1889-1900.
- Beninger JR (1987). Personalization of mass media and the growth of pseudo-community, Commun. Res. 14:352-371.
- Bone PF (1995). Word-of-Mouth Effects on Short-Term and Long-Term Product Judgments, J. Bus. Res. 32(3):213-223.
- Boon SD, Holmes JG. (1991). The dynamics of interpersonal trust: Resolving uncertainty in the face of risk, Cooperation and personal behavior, pp. 190-211.
- Boot AWA, Greedbaum SI, Thakor A (1993). Reputation and discretion in financial contracting. Am. Econ. Rev. 83(5):1165-1183.
- Cattell RB (1972). The 16 P.F. and basic personality structure: A reply to Eysenck, J. Behav. Sci. 1(4):169-187.
- Chang AM, Kannan PK, Whinston AB (1999). Consumers' extent of evaluation in brand choice, J. Bus. 72(2):229-251.
- Cheung CMK, Chiu PY, Lee MKO (2011). Online social networks: why do students use facebook? Comput. Human Behav. 27:1337-1343.
- Davis FD, Bagozzi RP, Warshaw PR (1989). User acceptance of computer technology: A comparison of two theoretical models. Manag. Sci. 35(8):982-1003.
- Deutsch M (1973). The Resolution of Conflict: Constructive and Destructive Processes, New Haven; Yale University Press.
- Dowling GR (1994). Corporate reputations: Strategies for developing the corporate brand, London: Kogan Page.
- Eisenbeiss M, Blechschmidt B, Backhaus K, Freund PA (2012). The (real) world is not enough: motivational drivers and user behavior in virtual worlds. J. Interactive Mark 26:4-20.
- Gefen D (1997). Building Users' Trust in Freeware Providers and the Effects of this Trust on Users' Perceptions of Usefulness, Ease of Use and Intended Use of Freeware, Georgia State University.
- Jarvenpaa SL, Knoll K, Leidner DE (1998). Is Anybody Out There? Antecedents of Trust in Global Virtual Teams. J. Manag. Inf. Syst.14(4):29-64.
- Jarvenpaa SL, Tractinsky N, Saarinen L, Vitale M (1999). Consumer trust in an Internet store: A cross-cultural validation. J. Computer-Mediated Commun. 5(2):1-35.
- Jung Y, Kang H (2010). User goals in social virtual worlds: A means-end chain approach, Comput. Human Behav. 26(2):218-225.
- Kannan PK, Chang AM, Whinston AB (1998). Marketing information on the way, Commun. ACM, 41(3):35-43.
- Kim DJ, Ferrin DL, Rao HR (2008). A trust based consumer decision making model in electronic commerce: The role of trust perceived risk and their antecedents. Decis. Support Syst. 44(2):544-564.
- Kim KK, Prabhakar B (2004). Initial trust and the adoption of B2C ecommerce the case of internet banking, the DATA BASE for Advances in Information Systems 35(2):50-64.
- Kuan HH, Bock GW (2007). Trust transference in brick and click retailers: an investigation of the before online visit phase. Inf. Manag. 44(2):175-187.
- Lee FSL, Vogel D, Limayem M (2002). Virtual community informatics: What we know and what we need to know, in the 35th Hawaii International Conference on Systems Sciences, Symposium held at the Hawaii.
- Lim KH, Sia CL, Lee MKO, Benbasat I (2006). Do I Trust You Online, and If So Will I Buy An Empirical Study of Two Trust-Building Strategies. J. Manag. Inf. Syst. 23(2):233-266.
- Lin J, Lu Y, Wang B, Wei KK (2011). The role of inter-channel trust transfer in establishing mobile commerce trust. Electron. Commer. Res. Appl. 10:615-625.
- Lu Y, Zhao L, Wang B (2010). Form virtual community members to C2C e-commerce buyers: trust in virtual communities and its effect on consumers' purchase intention. Electron. Commer. Res. Appl. 9:346-360.

- Malhotra NK, Kim S, Agarwal J (2004). Internet Users' Information Privacy Concerns (IUIPC): The Construct, the Scale, and a Causal Model. Inf. Syst. Res. 15(4):336-355.
- Mantymaki M, Salo J (2011). Teenagers in social virtual worlds: continuous use and purchasing behavior. Comput. Human Behav. 27:2088-2097.
- Moukas G, Zacharia PM, Pattie M (1999). Amalthaea and Histos:MultiAgent Systems for WWW Sites and Reputation Recommendations, in: M. Klusch (Ed), Intelligent Information Agent, Springer, pp. 293-322.
- Murray KB (1991). A test of services marketing theory: Consumer acquisition activities. J. Mark. 55(1):10-25.
- Resnick P, Zeckhauser R, Frendman E, Kuwabara K (2000). Reputation systems, Communications of the ACM 43(12):45-48.
- Rheingold H (1993). Virtual community: homesteading on the electronic frontier, Addison-Wesley.
- Sharif K J, Kalafatis SP, Samouel P (2005). Cognitive and behavioral determinants of trust in small and medium-sized enterprises. J. Small Bus. Enterprise Dev. 12(3):409-421.
- Whelan B (2005). Facebook, a fun resource or invasion of privacy. Athensnews.com. 08 September 2005. 27 <http://athensnews.com/issue/article.php3?story\_id=21491>.
- Wilson TD (2000). Human Information Behavior. J. Inf. Sci. Res. 3(2):49-55.

- Woo GK, Chang L, Stephen JH (2004). Effects of an online virtual community on customer loyalty and travel product purchases. Tourism Manag. 25:343-355.
- Wulf KD, Odekerken-Schroder G, Iacobucci D (2001). Investments in consumer relationships: A cross-country and cross-industry exploration. J. Mark. 65(4):33-50.
- Yang C (2011). Analysis on protection of e-commerce consumer network privacy. Procedia Engineering, 15:5519-5524.
- Yoo JH (1996). Asia's economic growth in the next decade: Opportunities and constraints. J. Asian Econ. 7(3):393-406.
- Young KS (1997). Internet Addiction: The Emergence of a New Disorder, Presented at the 1997 American Psychological Association Annual Conference.
- Zhao L, Lu Y, Wang B, Chau PYK, Zhang L (2012). Cultivating the sense of belonging and motivating user participation in virtual communities: a social capital perspective. Int. J. Inf. Manag.doi: 10.1016/j.ijinfomgt.2012.02.006. 32(6):574-588.

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Full Length Research Paper

# Effect of oxygen plasma treatments on the structural and optical properties of polyimide films

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A detailed study of some physical properties of Polyimide films after exposing them to oxygen plasma is presented. The structure of the sample has been analyzed by X-ray diffraction technique (XRD) and is found to be semi crystalline. Thermogravimetric Analysis (TGA) studies revealed that the thermal stability of polyimide films have improved after being exposed to oxygen plasma, at different time intervals, ranging from 1 to 5 min. Optical constants such as refractive index (n), extinction coefficient (K) and complex dielectric constant have been determined. A great dependence of the fundamental optical constants on the exposure time was noticed. Upon exposure to oxygen plasma, decrease in the refractive index was obtained. On the other hand the driving absorption coefficient ( $\alpha$ ) and consequently the optical band gap have been estimated. The real ( $\epsilon$ ) and imaginary parts ( $\epsilon$ ) of the dielectric constant have been determined. A great dependence of solution ( $\alpha$ ) and consequently the optical band gap have been estimated. The real ( $\epsilon$ ) and imaginary parts ( $\epsilon$ ) of the dielectric constant have been determined. The dispersion parameters such as E<sub>0</sub> (single-oscillator energy), E<sub>d</sub> (dispersive energy) and M<sub>-1</sub>, M<sub>-3</sub> (moments) were calculated and discussed.

**Key words:** Plasma deposition, X-ray diffraction (XRD), crystal structure, optical properties, thermogravimetric analysis (TGA).

#### INTRODUCTION

Polymer-based optical materials are particularly attractive in integrated optical waveguide devices because they can offer rapid processibility, cost-effectiveness, high yields, and high performance, such as smaller birefringence compared to silica. Furthermore, optical polymers provide an ideal platform for incorporation of more complex material functionalities through different doping or reaction agents, thereby enabling amplification and electro-optic effects to be achieved, once the passive optical polymer technology is established (Ma et al., Conventional optical 2002). polymers, such as polymethylmethacrylate (Kagami et al., 1995), polystyrene (Gokan et al., 1982) and polycarbonate (Singh et al., 1996) possess different structures and demonstrate many attractive properties, but not all of them possess the needed thermal stability for direct onchip interconnect applications.

Polyimide has found widespread applications in industry for insulation of electrical machines (Verdianz et al., 2006) as optical materials, for flexible print circuits (Choi et al., 2009). Polyimide based materials have also been applied as electrodes in biomedical micro-devices (Mercanzini et al., 2009).

In this regard, polyamides are a proven class

\*Corresponding author. E-mail: alyatta2001@yahoo.com, Tel: 02-22875924. Fax: (00202)22876031. Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> License 4.0 International License of polymers in the microelectronics industry due to their outstanding properties, especially for their high thermal stability. Polyimides (PIs) are a class of representative high performance polymers possessing the cyclic imide and aromatic groups in the main chains. At present, Polyimides (Pls) are extensively used in the microelectronics, photonics, optics, and aerospace industries not only for their very excellent thermal stability but also for their good mechanical properties, low dielectric constant, low coefficient of thermal expansion, and high radiation resistance. Significant effort has been expended to improve their properties further by modification of the chain backbones and higher-order structure control (Atta, 2013; Hasegawa and Horie, 2001). Due to its easy synthesis and attractive optical properties, polyimide is expected to play an important role in the field of organic optical waveguides.

Plasmas generated are widely used to activate polvimide properties. The properties are characterized by the modification of chemical and physical properties which is based on chain scission, the formation of functional groups, and cross-linking (Atta et al., 2014). The energetic electrons, ions, excited atoms, molecules, and UV photons present in the gas phase are responsible for the material modification, but their role in the interaction with the polymer is yet not fully understood due to the complexity of the gas phase and the polymer structure (Hasegawa and Horie, 2001). The polymer films are bombarded by the plasma active species mentioned above just described that leads to chain scissions and polymer degradation. If a plasma reactive gas is used, the appearance of new functional groups on the film will be expected. The most important feature of the plasma technique is the ability to control the modification of the polymer properties. Reactions between plasma species and polymer film make it possible to form polar groups on the film for instance C-O, C=O, O-C=O are chemically reactive and cause an increase of the surface energy and wetting qualities (Atta et al., 2013). Here, the intention of this study is to investigate the effect of oxygen exposure time on the polyimide films has been carried out using Xray Diffraction (XRD), Thermogravimetric Analysis (TGA) and optical properties.

#### EXPERIMENTAL

Polyimide (Kapton) films of thickness 160  $\mu$ m (Du Pont, USA) were used for oxygen plasma exposure process. We use the reactive ion etching (RIE) technique system with the following Oxygen plasma parameters, the working pressure is 7.3E<sup>-3</sup> mBar; Oxygen gas flow rate is 25 s/cm; and the incident power is kept constant at 100 W, with a corresponding DC self-bias voltage – 275 V and the exposure time varied from 0 to 5 min. The exposure process was performed using a Radio-Frequency (RF) of 13.56 MHZ at National Laboratory of Advanced Technology and Nano-Science (INFM-TASC), Trieste, Italy. Before performing the plasma treatment, the polyimide polymeric samples were first cleaned by acetone using ultrasonic technique in order to remove contamination on the polymeric surface. XRD scanning was carried out using fully

computerized X-ray diffractometer (Shimadzu type XD-DI). Filtered copper radiation,  $\lambda$ =1.542A was used in this investigation. The X-ray tube was operated at 40 kV and 30 mA anode current throughout the measurements. The pattern was recorded at a scanning rate of 4%min. The above operation conditions were maintained during all the relevant measurements. Hence, it is a plot of the intensity against the angle 2 $\theta$ , where  $\theta$  is the reflection angle of X-ray given in Bragg's equation  $2d \sin \theta = n\lambda$ . The thermal stability of the polyimide films was investigated by Thermo Gravimetric Analysis (TGA) (Shimadzu, Japan). The TGA measurements were carried out in N<sub>2</sub> atmosphere from room temperature to 500°C using a heating rate of 10°C/min.

Optical density of absorbance for the deposited and exposure films was measured over range of 200 to 2500 nm using Kontron – UV/VIS spectrophotometer (made in Switzerland). Different parts along the entire film were measured until good reproducibility of the respective absorption and transmission spectra was achieved. The obtained absorption data against incident light wavelength were used to calculate the electronic absorption coefficient ( $\alpha$  cm<sup>-1</sup>) and hence the optical energy gap as well as the volume and surface energy loss functions.

#### **RESULTS AND DISCUSSION**

## Oxygen plasma exposure effects on X-ray diffraction studies

The X-ray diffraction scans of "Polyimide films as a function of Bragg angle  $(2\theta)$  are displayed in Figure 1 for virgin and all oxygen plasma exposure time. The diffraction pattern of virgin polymer clearly indicates that this polymer is semi-crystalline in nature. The X-ray diffraction data of the virgin sample (Table 1) shows three peaks at  $2\theta$ = 14.88°, 21.78° and 26.255° with lattice spacing d = 5.94882Å, 4.0773Å and 3.39162Å, and the corresponding full widths at half maxima (FWHM) are 2.84°, 3.08° and 2.23°, respectively. The diffraction pattern of virgin sample showed partial crystallinity and the most intense peak appeared at  $2\theta$ = 26.255°. However, in case of increasing the plasma exposure, a significant change in the diffraction pattern has been observed (Table 1). The diffraction patterns of the virgin sample and exposed samples at different time are quite different and the three original peaks are found at slightly higher angular positions respectively. It is evident that the diffraction pattern of the exposure Polyimide is broader than the virgin one, which indicates a decrease in crystallinity. Similar finding was represented in (Qi et al. 2006 and Shalaby et al. 2013).

As shown in Table 2 by increasing the time of exposure to the oxygen plasma, there is always a possibility of development of strain (stress), which affects the mechanical properties of the samples such as the stability of microstructure, the strain (stress) in a sample can be intrinsic, caused by the conditions prevailing during deposition. On other hand, strain (stress) can be extrinsic to the sample but intrinsic to the composite – substrate system, caused by the difference in thermal expansion coefficient (Bin Ahmed et al., 2012). The



Diffraction angle  $(2\theta^{0})$  degrees

Figure 1. X- ray diffraction patterns spectra for polyimide film with oxygen plasma exposure time.

Table 1. The X-ray diffraction data for PI as a function of plasma exposure time.

Filme	First Peak		Second Peak		Third Peak				
FIIMS	d (A)	29	FWHM	d (A)	29	FWHM	d (A)	29	FWHM
Virgin Film	4.077	21.780	3.08	5.949	14.88	2.84	3.395	26.290	2.88
Exposed 1 min	4.065	21.846	2.93	6.021	14.70	2.29	3.392	26.270	2.26
Exposed 2 min	4.056	21.543	2.92	6.062	14.60	2.14	3.390	26.255	2.50
Exposed 3 min	4.001	22.340	2.82	6.106	14.53	2.11	3.387	26.243	2.22
Exposed 4 min	3.813	22.200	2.32	6.155	14.38	2.04	3.351	26.230	2.23
Exposed 5min	3.781	22.109	2.28	6.197	14.26	1.56	3.317	26.060	1.96

crystallite size and the residual strain are calculated from full width at half maximum (FWHM) using the relation (1) for all phases

$$P = \frac{K\lambda}{\beta\cos\theta} \ \beta = \frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta \ \delta = \frac{1}{D^2}$$
(1)

where ( $\beta$ ) is full width at half maxima (FWHM) in radians, the wavelength,  $\lambda$  of X-ray beam (1×5418 Å), *P* the crystallite size in A° and *K* is a constant for most cases it is close to 1. Assuming K = 1 in Equation (1), the crystallite sizes were calculated for strong peaks in all samples as given in Table 2. However, particularly in case of solid polymeric materials, the exact nature of the interrelation between spacing, crystallite size and the

<b>Films</b>	First Peak			Second Peak			Third Peak		
FIIMS	P(m) E-09	δ <b>Ε-16</b>	Δ (ε) <b>Ε-2</b>	P(m) E-09	δ	Δ (ε) <b>Ε-2</b>	P(m) E-09	δ	Δ (ε) <b>Ε-2</b>
Virgin Film	2.746	13.267	1.783	2.949	11.501	2.423	2.961	11.407	1.374
Exposed 1 min	2.884	12.030	1.693	3.651	7.500	1.980	3.773	7.025	1.194
Exposed 2 min	2.883	12.021	1.717	3.912	6.534	1.861	3.412	8.597	1.079
Exposed 3 min	3.002	11.100	1.591	3.973	6.335	1.841	3.841	6.779	1.066
Exposed 4 min	3.647	7.517	1.318	4.103	5.941	1.802	3.823	6.841	1.061
Exposed 5min	3.711	7.262	1.300	5.365	3.457	1.389	4.349	5.288	0.944

Table 2. The crystallite size for PI as a function of plasma exposure time.

Table 3. The interchain distance (r), interplaner distance (d) and the distortion parameter (g) for PI as a function of plasma exposure time.

Filmo	First Peak		Second Peak			Third Peak			
гшііз	<i>r</i> E-10	<i>d</i> E-10	g E-10	<i>r</i> E-10	<i>d</i> E-10	g E-10	<i>r</i> E-10	<i>d</i> E-10	g E-10
Virgin Film	5.101	4.081	0.279	7.442	5.954	0.38	4.237	3.390	0.215
Exposed 1 min	5.085	4.068	0.265	7.532	6.026	0.310	4.240	3.392	0.169
Exposed 2 min	5.156	4.124	0.269	7.584	6.067	0.292	4.243	3.394	0.187
Exposed 3 min	4.974	3.979	0.249	7.620	6.096	0.288	4.245	3.396	0.166
Exposed 4 min	5.005	4.004	0.206	7.699	6.159	0.282	4.247	3.397	0.167
Exposed 5 min	5.026	4.021	0.204	7.764	6.211	0.218	4.274	3.419	0.148

degree of disorder is yet to be understood in proper perspective. These bands agree with those elsewhere reported (Liu et al., 2002; Sahaet al., 2009)

The strain ( $\varepsilon$ ) was calculated from the slope of the ( $\beta cos \theta$ ) versus ( $sin \theta$ ) plot using the Equation (1). The dislocation density ( $\delta$ ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the Equation 1. Table 3 showed that the decrease in X-ray intensity may be resulting from grain size. This appears as boarding beaks, on the other hand, decreasing in the interchain distance (r) and the interplaner distance in the peaks lead to deceasing in crystallinty.

$$r = \frac{5\lambda}{8\sin\theta}$$
  $d = \frac{\lambda}{2\sin\theta}$   $g = \frac{\beta}{\tan\theta}$  (2)

Where interchain distance (r) and d is interplaner distance. Also, g is distortion parameter. From Table 2 it has been observed that the crystallite size decreases but strain and dislocation density in the samples increase with the increase in the time of exposure by oxygen. However, the decrease in intensity and the shift in angular position towards the higher angle can be explained by the decrease in lattice spacing (r and d). It also suggests a change in crystallite size of the samples exposed to oxygen plasma at different times. The crystallite sizes of the virgin and irradiated Polyimide-polymer have been calculated using Scherrer's equation

(Equation 1).

#### Thermogravimetric analysis (TGA)

Oxygen plasma exposure effects on the thermal stability of polymer were evaluated by TGA. TGA is a technique used to accurately track the *in situ* weight changes of a sample during the heating process, thereby providing information on thermal degradation. Figure 2a, b shows the TGA curves for deposited films and also exposed film at period 5 min. From Figure 2a, b, it is evident that the thermal oxidative degradation of the samples involved two different steps in the whole process. This is probably because the first step at 300°C (about 1.5% weight loss in TGA curve at this temperature) resulted in some decomposition and consequently hindered the crystallization of polyimide on the second step. It is clear that this polyimide exhibited excellent thermal stability, since no obvious weight loss was found in the differential thermogravimetric (TGA) curve below 500°C. This indicated that crystallization of the polyimide occurred rapidly during the thermal imidization of precursor, and semicrystalline polyimide can be readily obtained. The increase in the weight residues above 500°C illustrates successful incorporation of higher exposure period time (5 min of oxygen plasma) as shown in Figure 2b, and ultimately increases in thermal stability. The improvement of the thermal stability of the polyimide by increasing plasma exposure can be based on the fact that these



Figure 2. TGA curves for a-unexposed and b-exposed polyimide film with 5 min oxygen plasma.

materials have inherently good thermal stability and also due to the strong interaction/chemical bonding that exposed the polyimide film. These results suggest that molecules are bonding to the polyimide through reaction with H bonds and possibly through functionalities resulting from oxidative degradation of the polyimide film. The difference is mainly attributable to the different responses of the polymers to the evolution systems. One of the most important key parameters is the *T*GA of the optical device fabrication.

#### **UV-Visible spectrophotometric measurements**

Figure 3 shows the transmittance spectra, obtained at room temperature and near normal incidence for virgin film and different oxygen plasma exposure (1, 2, 3, 4 and 5 min) in the visible region. As can be seen from this Figure 3, the obtained films are characterized with high transmission greater than 60% for 600 nm depending on the film exposed by oxygen.

The transmittance decreases as the exposure time increases at wavelength  $\lambda = 600$  nm and it can be positively concluded that the material is of highly absorbing nature. The absorption coefficient was calculated from transmittance measurements with the aid of the expression (Kiryong and John, 2002).

$$\alpha = \frac{2.303}{d} \log_{10}(\frac{1}{T})$$
(3)

where d is the thickness of the film and T is the transmittance. If the sample faces are parallel, which is in most of the current case, multiple reflections have to be taken into account within the sample thickness. In this work, the polymer films are sufficiently thick compared to

the beam wavelength to neglect the interference phenomena. The air/polymer interface transmission T is expressed as functions of refractive index (n) and extinction coefficient (K) (Soldera et al., 200).

$$T = \frac{4n}{(n+1)^2 + k^2}$$
(4)

Once the measurements of value T is done, an iterative procedure to calculate n and K is initiated. When the absorption  $\alpha$  is known, the extinction coefficient K can be found the relation  $K = \frac{\alpha \lambda}{4\pi}$ . It is found that the value of n decreases, while the value of K increases with the photon energy at different time exposure. Oxygen plasma exposure has effect on the spectral dependence of (n) on wavelength  $\lambda$  for films as shown in Figure 4. The high-frequency properties for virgin film and films exposure by oxygen plasma could be treated by using Cauch's formula (Jenkins et al., 1985). It was found that the high-frequency dielectric constant  $\varepsilon_{\infty}$  can be determined from the plots of  $(n^2-1)^{-1}$  versus  $\lambda^{-2}$  as shown in Figure 5.

The Cauch's formula describes the contribution of free carriers and lattice modes. To obtain information about direct or indirect transitions, the optical band gap was determinate from analysis of the spectral dependence of the absorption near the fundamental absorption within the framework of an electron theory (Kumar et al., 2000). Thus, the electronic transition between valance and conduction band is given by

$$\alpha h \nu = A(h \nu - E_{\sigma})^{s} \tag{5}$$

Where s has discrete values like 1/2, 3/2, 2 or more



Figure 3. Transmission spectra for polyimide film with oxygen plasma exposure time.

depending on whether the transition is direct or indirect and allowed or forbidden. In the equation 5, A is constant, h is Plank's constant,  $E_g$  the optical band gap and  $h\nu$  the energy photon. Plotting  $(\alpha h\nu)^{1/2}$  as a function of the photon energy  $h\nu$  for the curves (un-exposed and exposed films) is shown in Figure 6. This liner region characterizes an optical gap  $E_g$  according to Equation 5. The linear region in Figure 6 is used to obtain the values of optical band gaps (namely  $E_g$ ). The values of  $E_g$  for all studied films are calculated and listed in Table 4. It is clear that the Polyimide film with thickness (0.160 mm) shows an energy gap  $E_g$ . And also, all films revealed an additional energy gap  $E_g$  at higher wavelength due to the decreased grain size of the higher time exposure films and also results in the decrease in crystalline nature which in turns decrease the band gap. Where, the peaks in UV-Vis region have generally interpreted in terms of  $\pi \rightarrow \pi^*$  transition between bonding and antibonding molecular orbital. Assuming that the frequency is relatively, the real part  $\varepsilon$  and imaginary part  $\varepsilon$ . Parts of the complex dielectric constant can be written according



Figure 4. Wavelength dependence of the refractive index *n* with oxygen plasma exposure time for polyimide film.

to the following relations (Wakkad et al., 2000).

$$\varepsilon = n^2 - K^2 = \varepsilon_{\infty} - \frac{e^2}{4\pi^2 C^2 \varepsilon_0} \frac{N}{m^*} \lambda^2$$
(6)

and

$$\varepsilon^{\sim} = 2nK = \frac{\varepsilon_{\infty}\omega_p^2}{8\pi^2 C^3 \tau} \lambda^3 \tag{7}$$

where

$$\omega_p = \left[ \frac{e^2 N}{\varepsilon_0 \varepsilon_\infty m^*} \right]^{\frac{1}{2}}$$
(8)

Where  $\omega_P$  is the plasma resonance frequency for one kind of the free carriers,  $\varepsilon_{\infty}$  is the high frequency dielectric

constant, e is the electronic charge, C is the velocity of light,  $\varepsilon_o$  is the free space dielectric constant, N /m<sup>\*</sup> is the ratio of free carrier concentration (N) to the free carrier effective mass (m<sup>\*</sup>) and  $\tau$  is the optical relaxation time.

Equations (6) to (8) were employed to determine the parameters  $\varepsilon_{\infty}$ ,  $\omega_p$  and N/m<sup>\*</sup>. The values  $\omega_p$  and N/m<sup>\*</sup> decreased by increasing oxygen plasma exposure time from 1 up to 5 min as shown in Figure 7. On the other hand, the shift of plasma edge towards higher frequency in the present case could be attributed to the relatively higher value of carrier concentration as mentioned before. This could be accounted for by the generation of excess electronic delocalized states.

The refractive index and the single oscillator parameters were calculated and discussed in terms of the Wemple-DiDmenico model (Wemple, 1973). That the parameters  $E_o$ ,  $E_d$  are calculated by know oscillator energy  $E_o$  which is independent of the scale of  $\varepsilon$  and is consequently an "average" energy gap, where as  $E_d$  depends on the scale of  $\varepsilon$  and thus serves as an



**Figure 5.** Plots  $(n^2 - 1)^{-1}$  against square wavelength  $(\lambda^{-2})$  with oxygen plasma exposure time for polyimide film.

interband strength parameters. Since the  $\rm M_{o}$  and  $\rm M_{d}$  moments are involved most heavily near the interband absorption edge.

The dispersion of refractive index below the interband absorption edge has been obtained according to the single oscillator model (Wemple, 1973; Wemple and Didomenico, 1971).

$$n^{2}(E) = 1 + \left[ \frac{E_{0}E_{d}}{E_{0}^{2} - E^{2}} \right]$$
(9)

where the parameters  $E_o$ ,  $E_d$  are the single-oscillator energy and dispersive energy respectively. By plotting  $(n^2 - 1)^{-1}$  versus  $E^2$  and fitting a straight line as shown in Figure 8,  $E_o$  and  $E_d$  are determined directly from the gradient,  $(E_o, E_d)^{-1}$  and the intercept  $(E_o / E_d)$ , on the vertical axis. Therefore, in order to account for the trend of  $E_d$ , it is suggested that the observed increase in  $E_d$  is with increasing exposed time is primarily a crosslinking. It is shown that a peculiarity for  $E_o$ ,  $E_d$ . On the basis of the above-mentioned model the single–oscillator parameters  $E_o$ ,  $E_d$  are related to the imaginary part,  $\epsilon$ `` of the complex dielectric constant, the M<sub>-1</sub>, M<sub>-3</sub> moments of polyimide can be derived from the relations (Yakuphanoglu et al., 2004)

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \text{ and } E_d^2 = \frac{M_{-1}^3}{M_d}$$
 (10)

So that the higher energy interband transitions that influence  $M_{.1}$  have little influence on  $E_{d}$ . However, within



Figure 6. The optical absorption coefficient edge plotted as  $(ahv)^{1/2}$  versus photon energy (hv) for un-irradiated and irradiated polyimide films with oxygen plasma exposure time.

Films	ε <sub>∞</sub>	ω <sub>p</sub> (10 <sup>12</sup> /s)	N/m* (10 <sup>17</sup> /cm <sup>3</sup> )	Eg (eV)
Virgin Film	1.836	9.831	6.911	1.328
Exposed 1 min	1.591	9.739	5.879	1.281
Exposed 2 min	1.512	9.691	5.534	1.266
Exposed 3 min	1.434	9.649	5.181	1.260
Exposed 4 min	1.351	9.639	4.890	1.241
Exposed 5 min	1.241	9.581	4.438	1.219

Table 4. The optical band gap  $E_g$  for PI as a function of plasma exposure time.

the confines of the constant conductivity model the equation 10 ( $M_{.1}$  /  $M_{.3}$ ) relates  $E_d$  to the sum-rule moments  $M_{.3}$  and  $M_{.1}$ . As a result, the dispersion energy may depend upon the detailed charge distribution within each unit cell, consequently, would then be closely related to chemical bonding may lie within a nearly localized orbital theory. Also, it was observed from Table 5 that  $E_0$  was increased while  $E_d$  was increased with the increasing plasma oxygen exposure time. Therefore, it is

suggested that the observed in  $E_d$  may be accounted for exposure sensitivity trend induced by increasing plasma oxygen exposure time.

#### Conclusions

1) XRD obtained for virgin and polyimide films were exposure by oxygen plasma as confirmed by the semi



**Figure 7.** Variation of  $\omega_p$  (plasma resonance frequency) with oxygen plasma exposure time for polyimide film.

crystalline nature for different films.

2) The intensity of these peaks for the exposed films is smallest than that of virgin film, indicating that the crystallinity becomes little obvious by increasing molecular weight.

3) The TGA curves of the virgin polyimide and exposure films at various time showed that the thermal stability

increased with increasing time exposure.

4) Oxygen plasma exposure of polyimide films in the different time range 1 to 5 min has been investigated as a potential technique of refractive index modulating optical elements. There was an increase in the refractive index via increasing plasma exposure in the dispersion energy.
5) Single oscillator energies in the polyimide films were significantly influenced by Oxygen plasma effects. It was



Figure 8. Plots (n<sup>2</sup> - 1)<sup>-1</sup> against square photon energy (E<sup>2</sup>) with oxygen plasma exposure time for polyimide film.

Films	E₀	Ed	<b>M</b> -1	М-з
Virgin Film	1.723	0.945	0.548	0.185
Exposed 1 min	1.736	1.094	0.631	0.209
Exposed 2 min	1.750	1.168	0.668	0.218
Exposed 3 min	1.757	1.229	0.699	0.227
Exposed 4 min	1.758	1.274	0.725	0.235
Exposed 5 min	1.765	1.395	0.790	0.254

**Table 5.** The single-oscillator energy and dispersive energy parameters for PI as a function of plasma exposure time.

an increase in the dispersion energy and discussed in terms of the Wemple-DiDmenico model.

6) High frequency dielectric constant ( $\epsilon_{\infty}$ ) and N/m<sup>\*</sup> ratio of free carrier concentration (N) to the free carrier effective mass (m<sup>\*</sup>) are significantly affected by the change with increasing plasma exposure time.

7) The effect of Oxygen plasma exposure on the optical band gap obtained. Moreover, there was a decrease in the optical energy gap with increasing exposure time up to 5 min.

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#### **Conflict of Interest**

The authors have not declared any conflict of interests.

#### REFERENCES

- Atta A (2013). Modification of the Surface Properties of Polyimide Films Using Oxygen Plasma Exposure. Arab J. Nucl. Sci. Appl. 46(5):115-123.
- Atta A, Abdel Reheem AM, Abdel Rahman MM (2014).Effects of Argon plasma and ion beam on the morphology and wettability of polyethylene terephthalate (PET). J. Eng. Technol. Res. 6(2):18-26.
- Atta A, Fawzy YHA, Bek A, Abdel-Hamid HM, Elokr MM (2013). Modulation of structure, morphology and wettability of PTFE surface by low energy ion beam irradiation. Nucl. Instr. Meth. Phys. Res B. 300:46–53.
- Bin Ahmad M, Gharayebi Y , SapuanSalit M, Zobir Hussein M, Ebrahimiasl S, Dehzangi A (2012). Preparation, Characterization and Thermal Degradation of Polyimide (4-APS/BTDA)/SiO<sub>2</sub> Composite Films. Int. J. Mol. Sci. 13:4860-4872.
- Gokan H, Esho S, Ohnishi Y (1982). Dry etch resistance of organic materials. J. Electrochem. Soc. 1:205.
- Singh S, Kapoor A, Misra SCK, Tripathi KN (1996). Optimization of waveguide parameters of< i> bisphenol A</i> polycarbonate. Solid State Commun. 100:503-506
- Hasegawa M, Horie K (2001). Photophysics, photochemistry, and optical properties of polyimides. Progress Polym. Sci. 26(2):259-335.
- Jenkins FA, White HE (1985). Fundamental of Optics, McGraw-Hill, London: P. 479.
- Kiryong H, John L (2002). Studies on the photodegradation of polarized UV-exposed PMDA–ODA polyimide films. J. Appl. Poly. Sci. 86:3072.
- Kumar GA, Thomas J, George N, Kumar BA, Radhknshnam P, Nampoori VPN, Vallabham CPG (2000). Optical absorption studies of free (H2Pc) and rare earth (RePc) phthalocyanine doped borate glasses. Phys. Chem. Glass. 41:89.

- Liu X, Yamanaka K, Jikei M, Kakimoto M (2000). Semicrystalline polyimides starting from AB-type monomers. Chem. Mater. 12:3885-3891.
- Ma H, Jen AKY, Dalton LR (2002). Polymer-based optical waveguides: materials, processing, and devices. Adv. Mater. 14(19):1339-1365.
- Kagami M, Ito H, Ichikawa T, Kato S, Matsuda M, Takahashi N (1995). Fabrication of large-core, high-Δ optical waveguides in polymers. Appl. Opt. 34(6):1041-6.
- Mercanzini A,Colin P, Bensadoun JC, Bertsch A(2009). IEEE Trans. Biomed. Eng. 56(7):1909.
- Qi K, Daoud WA, Xin JH, Mak CL, Tang W, Cheung WP(2006). Self cleaning Cotton. J. Mat. Sci. 16:4567-4574.
- Saha NK, Joshi SV (2009).Performance evaluation of thin film composite polyamide nanofiltration membrane with variation in monomer type. J. Membrane Sci. 342:60–69.
- Shalaby SE, Al-Balakocy NG, Abo El-Ola SM, Elshafei AM (2013). Effect of Surface Activation of Nylon-6 Fabrics by Plasma and Grafting With vinyl Monomers on Its Functional Finishing With TiO<sub>2</sub> Nanoparticles. J. Appl. Sci. Res. 9(3):1743-1753.
- Soldera A, Monterrat E (2000). Mid-infrared optical properties of a polymer film: comparison between classical molecular simulations, spectrometry, and ellipsometry techniques. Polymer. 43:6027-6035.
- Verdianz T, Simburger H, Liska R (2006). Surface modification of imide containing polymers I: Catalytic groups. Eur. Polym. 42(3):638-654.
- Choi MC, Wakita J, Ha CS, Ando S (2009)."Highly transparent and refractive polyimides with controlled molecular structure by chlorine side groups". Macromolecules. 42 (14): 5112.
- Wakkad MM, Shokr EKh, Mohamed SH, Wakkad MM (2000). Optical and calorimetric studies of Ge–Sb–Se glasses. J. Non- Crys. Solids . 265:157.
- Wemple SH (1973). Refractive-index behavior of amorphous semiconductors and glasses. Phys. Rev. B7:3767.
- Wemple SH, Didomenico M (1971). Behavior of the electronic dielectric constant in covalent and ionic materials. Phys. Rev. B3:1338-1351.
- Yakuphanoglu F, Cukurovali A, Yilmaz I (2004). Determination and analysis of the dispersive optical constants of some organic thin films. Phys. B: Condensed Matt. 351:53-58.

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Full Length Research Paper

# Characterization and determination of catechins in green tea leaves using UV-visible spectrometer

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In this paper, characterizations of pure major catechins and method for determination of total catechins in green tea leaves have been reported using UV-visible spectrometer. Most research activities have been focused on chromatographic methods, however spectrophotometirc method is preferred because of its rapidity, high accuracy, and reproducibility. The optical transition properties of Epigallocatechin Gallate (EGCG) and Epicatechin Gallate (ECG) in water, methanol, ethanol, acetonitrile and Epigallocatechin (EGC) and Epicatechin (EC) in water were measured. The results show that, EGCG has highest molar decadic absorption coefficient in methanol than in the other solvents. ECG has the highest absorption cross-section, transitional dipole moment, and oscillator strength of all the catechins in water. On the other hand, EGC has the least optical transition properties of all the catechins in water. Limits of detection (LOD) were comprised in the range  $3.1 \times 10^{-2}$ gmL<sup>-1</sup> to  $1.6 \times 10^{-1} gmL^{-1}$  and reproducibilities with RSD lower than 2%. After characterization of the electron transition, a method was developed for UV-Visible determination of total catechins. Using the developed method, the content of total catechins in Ethiopian and Sri Lanka green tea leaves at room temperature was determined. The result of the experiment indicates that, Ethiopian green tea leaves has the greater total catechins (17±0.01%) than Sri Lanka green tea leaves (7.17±0.12%).

Key words: Tea leaves, catechins, extraction, UV-visible spectrometer, optical transition properties.

#### INTRODUCTION

Tea is one of the most widely consumed beverages in the world after water (Castro et al., 2010). It is used not only as fresh drink but also as traditional herb which has many benefits for human health. Tea has attracted scientific attention for its anticancer and antioxidant activities (Hirota et al., 2002; Karori et al., 2007). There are two major kinds of tea, black tea and green tea, and they both contain caffeine (1 to 5%) with small amounts of other xanthine alkaloids (Amra et al., 2006). The main components of tea are polyphenolic compounds, the main quality parameters for teas, commonly known as catechins, which represent a group of compounds belonging to the flavonoid family. Catechins, may be contained in (5 to 27%) of the dried tea leaf (Leung and

\*Corresponding author. E-mail: tadelechad@yahoo.com Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> <u>License 4.0 International License</u> Foster, 1996), which are divided into four primary compounds epigallocatechin gallate (EGCG), epicatechin gallate (ECG), epigallocatechin (EGC), epicatechin (EC) (Amra et al., 2006; Salova et al., 2013). EGCG constituting (10 to 50%) of catechins and being the most potent due to its degree of gallation and hydroxylation (Pellilo et al., 2002). It is also the main subject of scientific study with regard to its potential health effects (Kanwar et al., 2012). Polyphenols in green tea are believed as excellent free radical scavengers. Several clinical studies have proved polyphenols to be active in cancer prevention in several ways. Polyphenols have also been recently recognized as functionally active molecules possessing antioxidant, anticancer, antimutagenic properties, as well as exerting protective effects against cardiovascular and other diseases (Michael, 1999; John, 2008). With regard to the toxicity of catechins, studies have shown no toxic effects in animals (Chengelis et al., 2008: Takami et al., 2008).

To determine these important tea components in tea, most research activities have been focused on chromatographic methods (Collier and Mallows, 1971; Khokhar and Magnusdottir, 2002; Wang et al., 2003). The methods give good separation of the catechins but they are time consuming and labor intensive (Guanqun et al., 2003). On the other hand, the UV-visible spectromerer method has been simple, fast and inexpensive and normally available in most laboratories. Furthermore, UVvisible spectrometric method is the best method to obtain total catehins in tea leaves. In the present method it is difficult to separate individual catechins in tea leaves.

In this study, we report a method for the determination of total catechins from green tea leaves. The method includes extracting them by water from green tea leaves and removing non-polar components by chloroform followed by determining its content by UV-visible spectrometer. The tea leaves studied in this research were Ethiopian and Sri Lanka green tea leaves. We have studied these two samples of tea leaves because they are the green tea leaves currently available in the Ethiopian supermarkets. In addition, the only green tea that has been produced in Ethiopia is Ethiopian green tea leaves and mostly the imported tea leaves and purchased in the Ethiopian supermarket is the Sri Lanka green tea leaves. The four major catechins were also characterized in water. Furthermore, EGCG and ECG were characterized in methanol, ethanol, and acetonitrile.

#### MATERIALS AND METHODS

#### Samples

Ethiopian and Sri Lanka green tea leaves were purchased from supermarkets in Addis Ababa. Sri Lanka green tea leaves (imported and distributed by: Kafco pvt. Ltd. Co., packed by: Qualitea Ceylon pvt. Ltd. Colombo, Sri Lanka). Ethiopian green tea (grown in high lands of Ethiopia, packed by Ethio Agri-ceft). Both of these samples were from tea bags.

#### Instrumentation

The absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer with wavelength range of 170 to 3200 nm. It consists of radiation source, monochormator, sample area, photometer, and detection area. There are two types of radiation sources. For the UV region, the radiation source is deuterium discharge lamp that emits polychromatic UV radiation which can then be filtered into monochromatic UV radiation. For the visible region, the radiation source is tungsten filament. The monochromator or wavelength selector disperses the light from radiation source into its separate wavelength. The radiation of only a particular wavelength leaves the monochromator through an exit slit. It has double monochromator which offers the advantage of low levels of stray light that is significant to measure a high value of absorbance using 1 cm cuvette. The monochromatic light that emerges from exit slit is pulsed by a chopper and split into sample and reference beam by the beam splitter. A reference beam passes through a sample holder or a quartz cuvette that contains only a solvent. The sample beam passes through a quartz cuvette that contains a sample solution. The radiation beams that passes through the detectors is amplified by difference amplifier and finally reaches the recorder, where the results are recoded digitally in a personal computer attached to a spectrometer. The investigated compound was measured in the UV-visible spectrum range of 200 to 500 nm with a spectral band width of 2 nm and scan speed of 240 nm min<sup>-1</sup>.

#### Chemicals

Chloroform (assay: 99.8%, European Union), methanol (assay: 99.8%, Indian), ethanol (assay: 96%, Indian), acetonitrile (assay: 99.99%, European Union), EGCG (M.W. 458.4 g/mol, Aldrich Germany), ECG(M.W. 442.4 g/mol, Aldrich Germany), EGC (M.W. 306.3 g/mol, Aldrich Germany), EC (M.W. 290.27 g/mol, Aldrich Germany).

#### Preparation of samples and standard solution

#### Standard solution preparation

For the determination of catechins in green tea leaves and for their characterization in distilled water, 1.06 mg of EGCG was immersed into 15 ml of distilled water and 0.46 mg of ECG, 0.87 mg of EGC and 0.38 mg of EC each immersed into 10 ml of distilled water and stirred for 1hr by magnetic stirrer. Absorbance versus wave length of each solution was taken by the UV-Visible spectrometer from which transitional properties of these compounds were calculated. EGCG and ECG were also characterized in methanol, ethanol and acetonitrile. For this 0.80, 0.55 and 0.88 mg of EGCG and 0.88, 0.55 and 0.61 mg of ECG each were immersed into 15 ml of methanol, ethanol, and acetonitrile respectively and stirred for 30min by magnetic stirrer and analyzed. These procedures were repeated for different concentrations. Finally, the molar decadic absorption coefficient, transitional dipole moment, oscillator strength, and integrated absorption coefficient were calculated.

#### Tea sample preparation

50mg of Ethiopian and Sri Lanka green tea leaves were added to 40 ml of distilled water at room temperature (to protect the epimerization of primary catechins). It was then stirred by magnetic stirrer for 1 h and filtered through glass filtrate. The tea infusion was washed by 40 ml of chloroform in a separatory funnel to remove caffeine, pigments, and other non-polar impurities. This step was



Figure 1. EGCG in water, methanol, ethanol, and acetonitrile.

repeated four times and negligible catechin compounds were found in the chloroform phase owing to their low solubility in chloroform. This was checked by taking the spectrum of chloroform phase until the absorption versus wavelength spectrum was flat when seen by the UV-Visible spectrometer. Then, the volume of water phase was measured. This solution was poured into 1 cm quartz cuvette and placed into the sample holder of the spectrometer and the spectrum was taken. To make the measurement more reliable three independent measurements were taken for each sample (n=3).

#### **RESULTS AND DISCUSSION**

The absorption spectra of pure catechins and catechins in tea leaves were measured using UV-visible spectrometer in the spectral range of 200 to 500 nm. The spectra were recorded at a spectral bandwidth of 2 nm and scan speed of 240 nm per minute. Each data in these experimental activities was found from computerized recorder interfaced with the spectrometer. It was then analyzed using origin 6.1 soft ware.

## UV-Visible absorbance of catechins in water, methanol, ethanol, and acetonitrile

The absorbance versus wavelength was measured by UV-visible spectrometer for each solution of known concentrations of catechins in water, methanol, ethanol, and acetonitrile. The absorption spectrums of catechins in water, methanol, ethanol, and acetonitrile are shown in Figures 1, 2, 3, and 4 respectively. From the spectra

(Figures 1, 2, 3 and 4), it can be observed that EGCG absorbs in the spectral range between 248 to 361 nm in water with  $\lambda_{\rm max}$  at 273.6 nm and in the other solvents, the spectral range is between 246 to 323 nm with  $\lambda_{\max}$ 276.0 nm in methanol and ethanol and 271.2 nm in acetonitrile. This indicates that, peak absorbance of EGCG in methanol and ethanol is the same but it is shifted to the shorter wave length (blue shifted) in the acetonitrile. The spectral range of ECG in water is from 246 to 363 nm with  $\lambda_{
m max}$  276.8 nm and from 246 to 325 nm in the other solvents with  $\lambda_{max}$  279.2 nm in methanol and ethanol and 273.6 nm in acetonitrile. Similar to that of EGCG, the maximum absorbance of ECG in methanol and ethanol is the same, and for acetonitrile  $\lambda_{\max}$  is shifted to the shorter wave length (blue shifted). The spectral range of EGC in water is between 254 to 378 nm and  $\lambda_{\max}$  at 269.6 nm and EC between 252 to 328 nm and  $\lambda_{\max}$  at 278.4 nm in water. In the region below the

 $\chi_{\rm max}$  at 276.4 mm m water. In the region below the minimum wave length of the band gap shows the region of solvent absorption.

## Optical transition properties of catechins in water, methanol, ethanol, and acetonitrile

The optical transition properties of catechins were calculated in solvents from their UV-visible spectra to



Figure 2. ECG in water, methanol, ethanol, and acetonitrile.



Figure 3. EGC in water.

(1)

compare the strength of transition. For incident light intensity  $I_0$ , propagating a distance / in the absorbing medium, the transmitted light intensity I can be described as:

Where  $a_{\lambda}$  is the absorption coefficient.

The Beer-Lambert law results directly from Equation (1) (Gunter and Tuan, 2003).

$$I = I_0 e^{-\varepsilon(v)cl}$$
 (2)

 $\mathbf{I} = \mathbf{I}_0 e^{-a_{\lambda} l},$ 



Figure 4. EC in water.

Where  $\varepsilon(v)$  is the molar decadic absorption coefficient and c is the concentration of the absorbing compound. The molar decadic absorption coefficient  $\varepsilon(v)$  represents the ability of a molecule to absorb light in a given solvent. The Beer-Lambert law is usually expressed in its logarithmic form:

$$\ln\left(\frac{I_0}{I}\right) = A = \varepsilon(v)cI,$$
(3)

Where A is the dimensionless quantity called absorbance, and  $I/I_0$  transmittance (T).

For n-multicomponent case, the relation becomes (Clark et al., 1993).

$$A_{\text{total}} = A_1 + A_2 + \dots + A_n. \tag{4}$$

The molar decadic absorption coefficient was calculated from Equation (3) at  $\lambda_{max}$  for EGCG and ECG in the four solvents and in water for EGC and EC. From Equation (1), the absorption coefficient is given by:

$$a_{\lambda} = \frac{1}{l} \ln \frac{I_0}{I}$$
<sup>(5)</sup>

An absorption band for a given transition usually extends over a range of frequencies, the integrated absorption coefficient. Thus, the integrated absorption coefficient  $a_t$ which is the sum of absorption coefficient for all frequencies in the band is expressed as:

$$a_t = \int a_\lambda d\nu \,, \tag{6}$$

Where  $\nu$  is the frequency.

The integrated absorption coefficient is independent of line function, which varies due to pressure, temperature, and solute solvent interaction. The integrated absorption cross-section  $\delta_t$  which characterize the photon-capture area of a molecule can be calculated by the following equation:

$$\delta_t = \frac{1}{N} \int a_\lambda d\nu \,, \tag{7}$$

Where N is the number density of the molecules.

The integrated absorption cross-section of catechins can be found by recalculating the absorbance versus wave number using origin 6.1 soft ware. The integrated area under the curve was obtained by integrating in the band gap for the catechins in each solvent. Figures 5, 6, 7, and 8 shows the spectra of absorption coefficient versus wavenumber of catechins in different solvents. The transitional dipole moment of the dissolved molecule, which is related to the molar decadic absorption coefficient by the integral absorption coefficient, is calculated by the equation (Liptay, 1969 and Michale, 1999):

$$I_{A} = \int_{band} \frac{\varepsilon(v)}{\overline{v}} d\overline{v} = \frac{1}{3} \frac{2h\pi^{2}Na}{\ln(10)c_{0}\varepsilon_{0}} \left|\mu_{fi}\right|^{2} = \frac{1}{3}S\left|\mu_{fi}\right|^{2}, \quad (8)$$



**Figure 5.**  $a_{\nu}$  versus  $\nu$  of EGCG in water, methanol, ethanol, and acetonitrile.



**Figure 6.**  $a_{\nu}$  versus  $\nu$  of ECG in water, methanol, ethanol, and acetonitrile.

Where S =  $2.9352 \times 10^{60}$  c<sup>-2</sup>mol<sup>-1</sup>. The transitional dipole moments of catechins were found by recalculating the absorbance versus wave length into  $\frac{\varepsilon(\nu)}{\nu}$  versus  $\nu$  using origin 6.1 soft ware along with Equation (8).

The other important parameter, which provides the relative strength of electron transition, is the oscillator strength (f). It is the average number of elections per atom that can be excited by the incident radiation. Oscillator strength related to molar decadic absorption



**Figure 7.**  $a_{\nu}$  versus  $\nu$  of ECG in water.



**Figure 8.**  $a_{\nu}$  versus  $\nu$  of EC in water.

coefficient by the following equation (Georgakopoulous et al., 2004; Radwan, 2007).

$$f = 4.32 \times 10^{-9} \frac{molcm^2}{L} \int \varepsilon(v) dv \,. \tag{9}$$

In electronic spectroscopy especially in organic molecules, the transition observed in UV-visible region is  $\pi^* \leftarrow \pi$ . Thus, for catechins the electronic type transition is  $\pi^* \leftarrow \pi$  and this transition is the cause for absorption.

Catechins	Solvent	Molar decadic absorption coefficient( $\mathcal{E}_{max}$ ) in m <sup>2</sup> mol <sup>-1</sup>	Integrated absorption cross section in cm mol <sup>-1</sup>	Transitional dipole moment in cm	Oscillator strength
	Water	1084±3.92	(106.74±0.34)10 <sup>-15</sup>	(13.54±0.02)10 <sup>-30</sup>	0.278±0.001
	Methanol	1342±7.60	(120.24±0.56)10 <sup>-15</sup>	(14.36±0.03)10 <sup>-30</sup>	0.314±0.001
5000	Ethanol	1313±1.41	(118.66±0.22)10 <sup>-15</sup>	(14.24±0.02)10 <sup>-30</sup>	0.309±0.001
EGCG Acetonitrile	Acetonitrile	1255±2.60	(99.90±0.31)10 <sup>-15</sup>	(12.93±0.02)10 <sup>-30</sup>	0.260±0.001
	Water	1430±3.01	(133.61±0.25)10 <sup>-15</sup>	(15.16±0.01)10 <sup>-30</sup>	0.347±0.001
	Methanol	1464±34.50	(117.60±3.40)10 <sup>-15</sup>	(14.16±0.21)10 <sup>-30</sup>	0.306±0.009
FCC	Ethanol	1329±11.45	(112.27±0.89)10 <sup>-15</sup>	(13.86±0.05)10 <sup>-30</sup>	0.292±0.002
ECG	Acetonitrile	1470±10.55	(117.06±0.89)10 <sup>-15</sup>	(14.01±0.05)10 <sup>-30</sup>	0.304±0.002
EGC	Water	184.13±1.18	(10.94±0.02) 10 <sup>-15</sup>	(4.28±0.004)10 <sup>-30</sup>	0.028±0.001
EC	Water	311±10.39	(20.21±0.50) 10 <sup>-15</sup>	(5.94±0.007)10 <sup>-30</sup>	0.053±0.001

Table 1. Optical transition properties of catechins in water, methanol, ethanol and acetonitrile.

Using the above equations, the optical transition properties of catechins in different solvents are summarized in Table 1. From the results of Table 1, it can be seen that, EGCG has highest and lowest molar decadic absorption coefficient in methanol and water respectively. ECG has the highest absorption crosssection, transitional dipole moment, and oscillator strength of all the catechins in water. On the other hand, EGC has the least optical transition properties of all the catechins in water.

#### Validation of the method

The calibration graph correlating the absorbance and concentration of pure catechins in water was constructed at the highest peak for concentration range of (1.85-15.46)10-8mol cm-3 for EGCG, (1.30-10.40)10-8mol cm-3 for ECG, (9.47-28.40)10-8mol cm-3 for EGC, and (4.36-13.09)10-8mol cm-3 for EC. The standard deviation was determined from linear fit of data points is 0.016, 0.0037, 0.0017, and 0.0070 for EGCG, ECG, EGC, and EC respectively and the linear regression coefficient is 0.99935, 0.99997, 0.99998, and 0.99912 for EGCG, ECG, EGC, and EC respectively. Therefore, good linear relationships were observed for a wide concentration range. This indicates that absorbance is directly proportional to concentration or in other wards Beer-Lambert law is valid. The limits of detection (LOD) were calculated from the peak to noise ratios for the four catechins in water and found out to be  $3.1 \times 10^{-2} gmL^{-1}$ ,  $4.2 \times 10^{-2} gmL^{-1}$ ,  $1.6 \times 10^{-1} gmL^{-1}$  and  $9.5 \times 10^{-2} gmL^{-1}$  for ECG, EGCG, EGC, and EC respectively. The low LOD indicates that UV-Visible spectrometer is reliable for analyzing catechins in tea samples.

In Figure 9, the absorption spectra of the combination of pure catechins and catechins extracted by chloroform are similar. This indicates that, chloroform can be used to extract catechins from tea leaves.

#### Determination of catechins in tea leaves

A method was developed to determine catechins in tea leaves using UV-visible spectrometer. The method includes, first dissolving tea leaves in distilled water and removing caffeine, pigments, and other non- polar impurities using chloroform as mentioned in the procedure part. In this experimental activity, total catechin was determined using Beer's law. First, molar decadic absorption coefficient ( $\mathcal{E}_{max}$ ) at the maximum peak of the extracted real tea leaves was calculated from pure substances of the four catechins, EGCG, ECG, EGC, and EC, and total molar decadic absorption coefficient  $\varepsilon$  was then calculated. Total concentration c was then found from Beer's law (c =  $A/ \varepsilon I$ ), where A is maximum absorbance of real tea leaves and / length of the cuvette which is 1 cm. Total mass was then calculated using this concentration value (m = cMV), where M is the molecular weight and V is the volume. Finally, percentage of total catechins was determined. To make the result more reliable, three independent experiments were carried out for each sample (n=3). Table 2 presents the experimental result for the determination of catechins for the green tea leaves of Ethiopian and Sri Lanka origin.

The result of the experiment indicates that, the content of total catechins in Ethiopian green tea leaves is greater than Sri Lanka green tea leaves. This result agrees with the range of result reported by Leung and Foster (1996). Specifically, the result obtained in this research for



Figure 9. Absorption spectrum of catechins extracted from green tea leaves and catechins from pure substances.

Table 2. Experimental result of determination of catechins in green tea leaves (n = 3).

Sample	$\lambda_{ m max}$ (nm)	A <sub>max</sub>	Percentage of catechins
Ethiopian green tea leaves	272.8±0.0	0.6969±0.03	17.14±0.01
Sri Lanka green tea leaves	270.9±0.2	0.4311±0.02	7.17±0.12

Ethiopian tea leaves was almost similar to the result obtained using HPLC for different samples of tea leaves reported by Quan et al. (2006) in which percentage dried weight of total catechins of maximum 20.49 and minimum 14.32. The results found for the green tea extract followed this same sequence in which the total catechin content was 4 to 45% on average (Dalluge et al., 1998; Khokhar. Magnusdottir, 2002; Mizukami, Sawai. Yamaguchi, 2007). Studies suggest the consumption of 4 to 7 cups of green tea per day in order to obtain the expected health benefits of catechins. Precision of the method was determined by three replications of each sample. The precision (%RSD) of the replications was found to be less than two (0.06% for Ethiopian green tea leaves and 1.7% for Sri Lanka green tea leaves) which is indicative of a precise method.

#### Conclusions

A new method was presented to determine total

catechins in tea leaves and could be successfully applied for the analysis of real tea samples. Therefore, in this research content of total catechins in Ethiopian and Sri Lanka green tea leaves were determined by the developed method using UV-visible spectrometer. The range of results found in the literature was compared with the results found in this method which came to be noticeably similar. The result of the experiment indicates that, Ethiopian green tea leaves have greater catechins content than Sri Lanka green tea leaves purchased in Ethiopia. So, we can say that one can get more catechins from Ethiopian green tea leaves than Sri Lanka green tea leaves purchased in the same country.

Absorbance versus wavelength of the four pure major catechins (EGCG, ECG, EGC and EC) were taken in water and in addition, EGCG and ECG in methanol, ethanol, and acetonitrile. From the spectra it was found that, peak absorbance of EGCG and ECG in methanol and ethanol is the same but it is shifted to the shorter wavelength (blue shifted) in acetonitrile. As it is expected, the absorption maximum of acetonitrile, that cannot form hydrogen bond with solute is blue shifted. Optical transition properties of pure major catechins were also calculated in water. In addition, EGCG and ECG were calculated in methanol, ethanol, and acetonitrile, which can be used as reference for further studies.

#### **Conflict of Interest**

The authors have not declared any conflict of interest.

#### REFERENCES

- Amra PU, Mojca S, Zelijlo K, Bernd W, Frank O, Sabine G (2006).Extraction of active ingredients from green tea (*Camellia sinensis*): Extraction efficiency of major catechins and caffeine. Food Chem. 96:597-605.
- Castro J, Pregibon T, Chumanov K, Marous RK (2010). Determination of catechins and caffeine in proposed green tea standards reference materials by liquid chromatography-particle beam/electron ionization mass spectrometry (LC-PB/EIMS). Talanta. 82(5):1687-1695.
- Chengelis CP, Kirkpatrick JB, Regan KS, Radovsky AE, Beck MJ, Morita O, Tamaki Y, Suzuki H (2008). 28-Day oral (gavage) toxicity studies of green tea catechins prepared for beverages in rats. Food Chemical Toxicol. 46 978 – 989.
- Clark BJ, Frost T, Russel MA (1993). UV spectroscopy techniques instrumentation and data handling. Chapman and Hall, London. 4.
- Collier PD, Mallows R (1971). The estimation of flavanols in tea by gas chromatography of their trimethylsilyl derivatives. J. Chromatogr. 57:29-45.
- Dalluge JJ, Nelson BC, Thomas JB, Sander LC (1998). Selection of column and gradient eluition system for the separation of catechins in green tea using high-performance liquid chromatography. J. Chromatogr A. 793(2):265-274.
- Georgakopoulous S, Grondelle RV, Zwan GVD (2004). Circular dichroism of carotenoides in bacterial light-harvesting complexes: experimental and modeling. Biophys. J. 87:3010-3022.
- Guanqun S, Jinming L, Feng Q, Hule CW (2003). Extraction of catechins and caffeine from different tea leaves and comparison with micellar electrokinetic chromatography. Chinese Science B. 48(22):2438-2443.
- Gunter G, Tuan VD (2003).Handbook of spectroscopy. Wiley-VCH Verlag GmbH 1& CO KGa A.Weinheim ISBN 3 527- 29782 0.
- Hirota F, Masami S, Kazue I, Kei N (2002).Green tea: Cancer preventive beverage and/or drug. Cancer Letters. 188:9-13.

- John HW (2008). Tea and health: a historical perspective. Cancer Letters. 114:315-317.
- Kanwar J, Taskeen M, Mohammad I, Huo C, Chan TH, Dou QP (2012). Recent advances in tea polyphenols. Frontiers in Bioscience. 4:111-131.
- Karori SM, Wachira FN, Wanyoko JK, Ngure RM (2007). Antioxidant capacity of different types of tea products. Afr. J. Biotechnol. 6:2287-2296.
- Khokhar S, Magnusdottir SGM (2002). Total phenol, catechin and caffeine contents of teas commonly consumed in the United Kingdom. J. Agric. Food Chem. 50(3):565-570.
- Leung AY, Foster AY (1996).Encyclopedia of common natural ingredients used in food and their effects on health. American chemical society. pp.114-120.
- Liptay W (1969). Electrochromism and solvatochromism. Angewandte Chemie, International Edition. 8(3):177-187.
- Michael DB (1999). Green tea (Camellia sinensis) extract and its possible role in the prevention of cancer. ND Alternative Med. Rev. 4:5.
- Michale JL (1999). Molecular spectroscopy. USA Prentice- Hall, Inc. pp. 160-161.
- Mizukami Y, Sawai Y, Yamaguchi Y (2007). Simultaneous analysis of catechins, Gallic acid, strictinin, and purine alkaloids in green tea by using catecol as an internal standard. J. Agric. Food Chem. 55:4957-4964.
- Pellilo M, Bendini AB, Toschi GT, Vanzini M, Lercker G (2002). Preliminary investigation into development of HPLC with UV and MS –Electroscopy detection for analysis of tea catechins. Food Chem. 78:369-374.
- Quan PT, Hang TV, Hai Ha N, De NX, Tuyen TN (2006). Microwaveassisted extraction of polyphenols from fresh tea shoots. Science and Technology Development. 9:8.
- Radwan RM (2007). Electron induced modifications in the optical properties of polypropylene. J. Phys D Appl. Phys.40:374-379.
- Salova N, Carole CB, Aziz A, Jean-Louis M (2013). Tyrosinase Biosensor used for the determination of catechin derivatives in tea; Correlation with HPLC/DAD method. Food Nutr. Sci. 4:108-118.
- Takami S, Imai T, Hasumura M, Cho YM, Onose J, Hirose M (2008). Evaluation of toxicity of green tea catechins with 90-day dietary administration of F344 rats. Food Chem. Toxicol. 46(6):2222-2224.
- Wang HF, Provan GJ, Helliwell K (2003). HPLC determination of catechins in tea leaves and tea extracts using relative response factors. Food Chem. 81(2):307-312.

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