A STUDY ON THE REACTIVITY AND PHYSICOCHEMICAL PROPERTIES OF COATINGS BASED ON ACRYLATED BLACK SEED OIL COATINGS THROUGH CROSSLINKING AT AMBIENT TEMPERATURE

NGHIÊN CỨU KHẢ NĂNG PHẢN ỨNG VÀ TÍNH CHẤT CƠ LÝ CỦA LỚP PHỦ TRÊN CƠ SỞ DẦU HẠT CÂY ĐEN ACRYLAT HÓA BẰNG PHƯƠNG PHÁP KHÂU MẠCH Ở NHIỆT ĐỘ THƯỜNG

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ABSTRACT

Environmentally friendly organic coatings which are water-based, have low or no solvents and good physical properties based on the use of acrylate monomers/acrylate oligomers originating from vegetable oils are gaining attention as we move towards sustainable chemistry. Using thermal methods with acrylate and methacrylate monomers in the presence of initiators produces transparent films. An analysis on the influence of the nature of initiators shows that the activity of initiators is arranged in the order: D.1173 > PI.907 > I.184 > TPO > PI.PB, and the content of D.1173 initiators at 3% of the reaction occurs quickly after 3 hours at 40°C, producing a tightly crosslinked transparent film. The reactivity and properties of the coatings formed by acrylated black seed oil at ambient temperature have been studied using internal calibration, testing relative hardness, gel content, swelling ratio, impact resistance, and gloss. The research results provide a basis for the development of advanced, environmentally friendly organic coatings using black seed oil - a type of vegetable oil with naturally-epoxidized groups native to Vietnam.

Keywords: *Acrylated black seed oil, thermal crosslinking, organic coatings, initiators.*

TÓM TẮT

Lớp phủ hữu cơ thân thiện môi trường, ít hoặc không có dung môi, gốc nước và có tính chất cơ lý tốt trên cơ sở sử dụng các monome acrylat/oligome acryla có nguồn gốc từ dầu thực vật ngày càng được chú trọng để hướng tới hóa học bền vững. Các monome acrylat và metacrylat phương pháp nhiệt với sự có mặt của chất khơi mào tạo ra mang trong suốt. Phân tích ảnh hưởng của bản chất chất khơi mào cho thấy, hoạt tính của chất khơi mào được sắp xếp theo thứ tự: D.1173 > PI.907 > I.184 > TPO > PI.PB và hàm lượng chất khơi mào D.1173 3% phản ứng xảy ra nhanh sau 3 giờ ở 40°C, màng trong suốt tạo mạng lưới chặt chẽ. Khả năng phản ứng và các tính chất của lớp phủ tạo bởi dầu hạt cây đen acrylat ở nhiệt độ thường đã được nghiên cứu bằng phương pháp nội chuẩn, thử nghiệm độ cứng tương đối, phần gel, độ trương, độ bền va đập và độ bóng. Kết quả nghiên cứu là cơ sở để đưa dầu hạt cây đen - một loại dầu thực vật có nhóm epoxy tự nhiên ở Việt Nam cho sự phát triển lớp phủ hữu cơ tiên tiến, thân thiện môi trường.

Từ khóa: *Dầu hạt cây đen acrylat hóa, khâu mạch nhiệt, lớp phủ hữu cơ, chất khơi mào.*

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1. INTRODUCTION

Organic coatings are crucial in improving the surface properties of materials like metals, wood, plastics, and concrete. In addition to aesthetic enhancements, these coatings safeguard materials from environmental factors and adhere to stringent environmental regulations [1]. The global coating industry faces the imperative to minimize pollutant waste, compelling a shift toward eco-friendly solutions [2]. Water-borne dispersed coatings, employing crosslinking systems through methods such as photopolymerization, demonstrate environmental consciousness, energy efficiency, and high selectivity. Integrating photopolymerization and thermal crosslinking methods with vegetable oils offers a "green method" to address contemporary challenges in the organic coating sector [3, 4]. The crosslinked organic coating system which comprises monomers, oligomers or multifunctional polymers, initiators or catalysts has a rapid reaction, quickly transitioning the coating from a liquid to a solid state. The reactivity and properties of the coating formed depend on the proportions of constituents, chemical nature, temperature, curing intensity, and time [5-9]. However, manufacturing thick coatings and determining relationships within the reaction system for practical applications pose ongoing challenges for researchers and manufacturers.

Vegetable oil mainly consists of triglycerides, which contains some reactive functional groups such as double bonds, hydroxyl groups, and active epoxy groups. Developing an organic coating system with acrylated vegetable oil through photopolymerization and thermal crosslinking methods is currently being focused on for research and development both domestically and internationally. Acrylated black seed oil is obtained through the ring-opening reaction of acrylic acid and methacrylic acid with black seed oil - a type of vegetable oil with naturally-epoxidized groups native to Vietnam [10]. Despite the tropical climate conducive to oil-bearing plants' growth, it exacerbates metal corrosion and material degradation. Thus, the investigation and development of new organic coatings utilizing acrylated black seed oil through crosslinking methods contribute significantly to corrosion mitigation and material preservation. This paper presents research results on the reactivity and physicochemical properties of coatings based on acrylated black seed oil utilizing various initiators through crosslinking methods at ambient temperature.

2. EXPERIMENT

2.1. Chemicals

- Acrylated black seed oil: DHCĐA2.0 (2.0mol acrylate/mol molecular weight), DHCĐA1.6 (1.6 mol acrylate/mol molecular weight), DHCĐMA1.6 (2.0mol methacrylate/mol molecular weight), and DHCĐA1.0 (1.0 mol acrylate/mol molecular weight), synthesized at the Rubber and Natural Resin Laboratory, Institute of Thermal Science - Vietnam Academy of Science and Technology.

- Primary initiators:

+ α-hydroxylxyclohexylphenylmetanon (I-184) from Ciba Geigy.

+ Diphenyl methanol (BP) from MERCK.

+ (Diphenylphosphoryl)(2,4,6-trimethylphenyl) methanone (TPO) from BAFS.

+2-methyl-1-[4-(methylsulfanyl)phenyl]-2-(morpholin-4-yl)propan-1-one (PI.907).

+2-hydroxy-2-methyl-1-phenylpropan-1-on (D.1173) from MERCK.

- Solvent: PA-grade chloroform from China.

2.2. Formation of crosslinking systems and sample fabrication

- The crosslinking system was created by thoroughly mixing the components: acrylated black seed oil, primary initiators in specified weight ratios, forming a film with a 20µm thickness. Subsequently, the film was dried at temperatures of 30, 35, 40, and 45°C in a drying oven. At specific intervals, samples were taken, and infrared to ascertain key parameters such as gel content, swelling ratio, and mechanical properties.

- The crosslinking membrane was created on the surface of KBr pellets with a 20µm thickness for infrared spectrum analysis on glass surface, on CT3 steel surface, on copper surface with a 30µm thickness to determine relative hardness, gel content, swelling ratio; impact resistance and adhesion; flexibility.

2.3. Methods of analyzing and testing

2.3.1. Infared spectrum analysis

The transformation of functional groups during the crosslinking process is determined using infrared spectroscopy on the FT-IR instrument, NEXUS 670, Nicolet (USA) at the Institute of Tropical Technology, Vietnam Academy of Science and Technology. The content of acrylate double bonds in acrylated black seed oil is quantitatively determined by an internal calibration method based on the specific absorption at 1410 cm-1 compared to the absorption intensity at 2927cm^{-1}, which is distinctive of the stretching modes of saturated C-H bonds, remaining unchanged during the reaction [11].

2.3.2. Determination, analysis of gel content and swelling ratio

The sample with initial mass m_1 after solidification was immediately immersed in chloroform for 24 hours. After removing the sample, its mass m_2 was measured then dried until a constant mass m_3 was achieved.

The gel content and swelling ratio are calculated by the following formulas:

$$\text{Gel content (\%)} = \frac{m_3}{m_1}.100$$

$$\text{Swelling ratio (\%)} = \frac{m_2}{m_3}.100$$

Where: m_1: Initial sample mass (g).

m_2: Mass of the sample soaked in chloroform for 24 hours before drying (g).

m_3: Remaining mass of the sample after drying (g).

2.3.3. Determination of the physicochemical properties

- The impact resistance of the sample is determined using the Impact Tester, model 304 from Germany, ISO 6272 standard, at the Institute of Tropical Technology, Vietnam Academy of Science and Technology.

- The adhesion of the sample is determined using the Elcometer Cross Hatch Cutter from the UK, ISO 2409 standard, at the Institute of Tropical Technology, Vietnam Academy of Science and Technology.

- The flexural strength of the sample is determined using the ШГ-1 apparatus, GOST 6806-53 standard, at the Institute of Tropical Technology, Vietnam Academy of Science and Technology.

3. RESULTS AND DISCUSSION

3.1. The effect of temperature on the crosslinking reaction and physical properties of the coating film

The effect of temperature on the crosslinking process of the DHCĐA2.0/D.1173 system with a ratio of 100/3 was conducted at reaction temperatures of 30°C, 35°C, 40°C, and 45°C.

The infrared spectra of the DHCĐA2.0/D.1173 = 100/3 crosslinking systems at different temperatures before and after 3 hours of crosslinking are presented in Fig. 1.

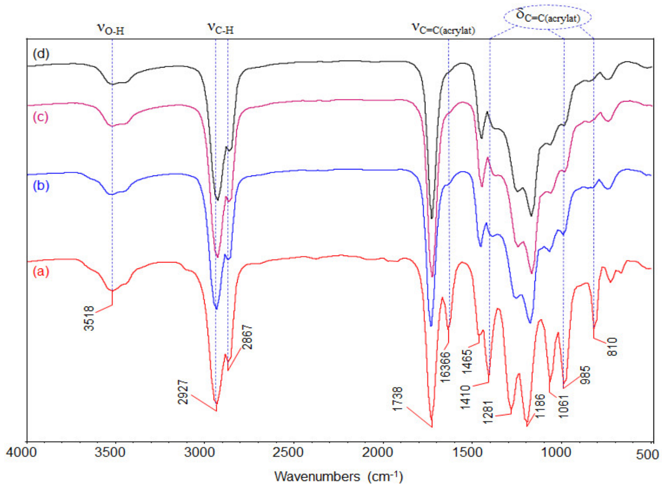


Figure 1. The infrared spectra of the thermal crosslinking system DHCĐA2.0/D.1173 = 100/3 before (a) and after 3 hours of reaction at 30°C (b), 35°C (c), and 40°C (d).

Observing from Fig. 1, the distinctive absorption for the stretching modes of CH bonds at 2927cm^{-1}, as well as its intensity, remains nearly unchanged. However, the distinctive absorptions for the acrylate groups at 1636cm^{-1}, 1410cm^{-1}, 985cm^{-1}, and 810cm^{-1} decrease significantly during the reaction [11]. Therefore, in our study, we utilized the internal calibration method to quantitatively determine the transformation of the acrylate functional groups during the crosslinking process at different temperatures.

- The transformation of acrylate groups during the reaction at different temperatures in the crosslinking process is presented in Fig. 2.

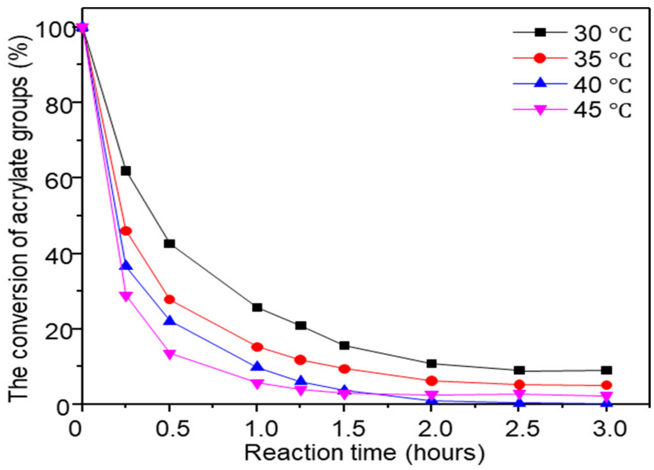


Figure 2. The transformation of acrylate groups during the thermal crosslinking process of the DHCĐA2.0/D.D.1173 = 100/3 system at temperatures of 30 (●), 35 (▲), 40 (■) và 45 (♦)

Observing from Fig. 2, the proportional increase in the rate of acrylate group conversion as the temperature ascends from 30°C to 45°C. Specifically, at 30°C and 35°C, after 3 hours of reaction, the acrylate group conversion reaches 91% and 95%, respectively. At 45°C, the acrylate group conversion rapidly reaches 96% after 1.25 hours, remaining almost unchanged after 3 hours of reaction. Notably, at 40°C, the acrylate group conversion completes after 2.5 hours, with a moderate reaction rate that is easy to control, and this temperature is also commonly encountered during the summer in Vietnam. Therefore, the temperature of 40°C is chosen to create the film for studying its properties as well as other influencing factors.

- The gel content and swelling ratio of the studied coatings are presented in Fig. 3.

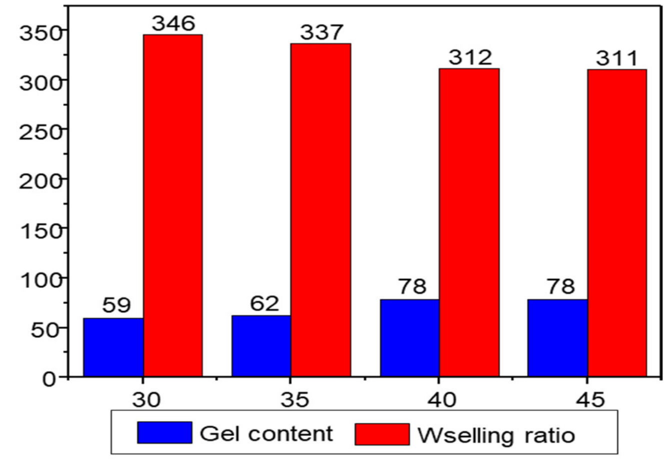


Figure 3. The values of gel content and swelling ratio of the coating system DHCĐA2.0/D.1173 = 100/3 at temperatures of 30, 35, 40, and 45°C after 3 hours of reaction

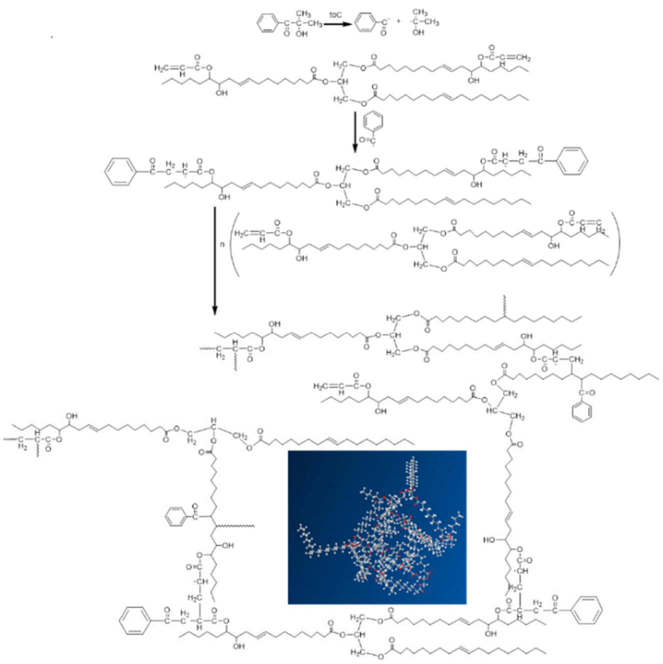


Figure 4. Crosslinking reaction of acrylated black seed oil at 40°C

Observing from Fig. 3, after 3.0 hours of reaction at 40°C and 45°C, the system has the highest gel content at 78%. At 30°C and 35°C, after immersing in the solvent for 24 hours, the film exhibits shrinkage and wrinkling, with corresponding gel contents of 59% and 62%. At 40°C, the high conversion efficiency of acrylate groups leads to a tightly crosslinked three-dimensional network. The film becomes solid, rigid, and almost insoluble.

3.2. The influence of initiators on the crosslinking reaction and physical properties of the coating

The influence of initiators on the crosslinking reaction of the researched system was conducted under the condition of the DHCDA2.0/initiator ratio of 100/3 at 40°C using initiators PI.PB, TPO, I.184, PI.907, and D.1173.

- The transformation of acrylate groups during the thermal crosslinking process with different initiators is presented in Fig. 5.

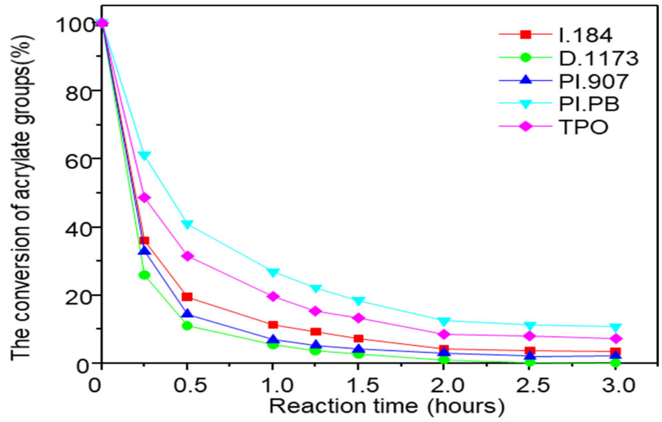


Figure 5. Transformation of acrylate groups in the DHCDA2.0/initiator system = 100/3 at 40°C

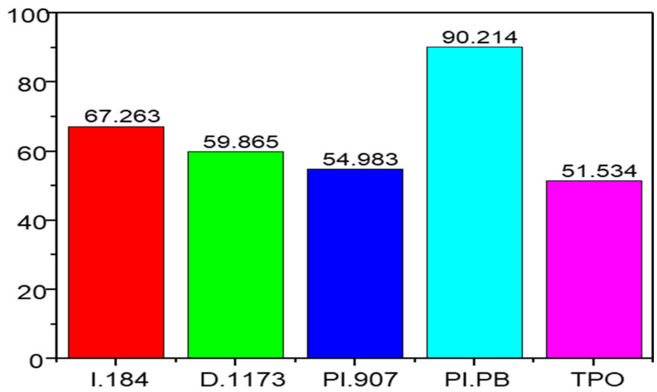


Figure 6. Bond dissociation energy of some initiators

Observing from Fig. 5, the initiators PI.PB and TPO exhibit low transformation of acrylate groups in the studied sample, while the initiators I.184, PI.907, and

D.1173 show higher transformation rates [5, 12]. The highest transformation of acrylate groups is recorded when using initiators D.1173, I.184, PI.907, TPO, and PI.PB at a concentration of 3%, with transformation rates of 100%, 98%, 96%, 91%, and 89%, respectively. Comparing the activity of these five initiators at the same concentration of 3%, their activity can be arranged in the following order: D.1173 > PI.907 > I.184 > TPO > PI.PB.

This is explained by the notion that initiators belonging to the aromatic ketone group form efficient benzoyl radicals for polymerization reactions. Meanwhile, benzophenone generates free radicals by abstracting a hydrogen atom from a molecule. The efficiency of benzophenone in generating free radicals is lower than that of aromatic ketone initiators. Free radicals formed from hydrogen abstraction are also weaker than benzoyl radicals. Therefore, the initiation efficiency of benzophenone is lower than that of aromatic ketone initiators used in the study. The an alysis results show that the initiator D.1173 achieves complete conversion of acrylate groups.

The physicochemical properties of the crosslinking system at 40°C with different initiators after 3 hours of reaction are presented in Table 1.

Table 1. Physical properties of the crosslinked system at 40°C with different initiators after 3 hours of reaction

Crosslinked system / Physicochemical property	Initiator				
	PI.PB	TPO	I.184	PI.907	D.1173
Gel content (%)	63	65	79	76	82
Swelling ratio (%)	424	397	307	318	296
Relative hardness	0.30	0.32	0.42	0.41	0.44
Impact resitance (kG.cm)	54	62	89	85	91
Gloss 60° (%)	83	100	97	100	100

- The influence of the content of the initiator

The influence of the content of the initiator D.1173 on the crosslinking reaction at 40°C of the system DHCĐA2.0/D.D.1173 is presented in Fig. 7.

Observing from Fig. 7, when the content of the initiator D.1173 is changed from 1% to 5%, the acrylate group content decreases rapidly in samples containing 3%, 4%, and 5% initiator content, reaching complete conversion after 3 hours of reaction [11]. Samples containing 1% and 2% D.1173 initiators have acrylate group conversion values of 87% and 89%, respectively. Increasing the initiator concentration from 3% to 5% does not significantly increase the rate of acrylate group conversion, and the final conversion of acrylate groups is complete for all concentrations. Therefore, the initiator D.1173 with a concentration of 3% is chosen as the initiator for the acrylated black seed oil reaction system.

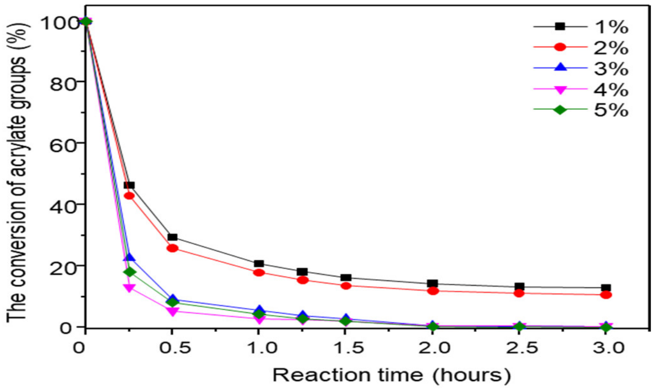


Figure 7. The effect of the content of the initiator D.1173 on the conversion of acrylate groups

3.3. The effect of acrylate groups on the crosslinking reaction and physical properties of the coating

Black seed oil acrylated with acrylic acid (HDCDA 2.0, HDCDA 1.6, HDCDA 1.0) and methacrylic acid (HDCDMA 1.6) were introduced into the crosslinking system to investigate the influence of the nature and content of acrylate groups on the crosslinking reaction.

The transformation of acrylate groups in the studied samples with different acrylate group contents during the crosslinking process at 40°C is presented in Fig. 8.

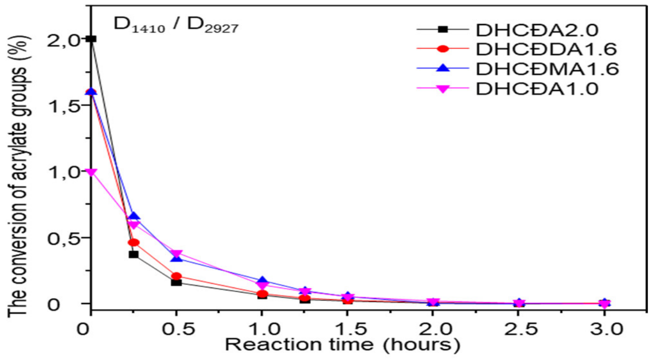


Figure 8. Transformation of acrylate groups in samples with different acrylate group contents during the crosslinking process at 40°C

Observing from Fig. 8, the acrylate groups of all samples undergo rapid transformation within the first hour of the reaction, followed by a gradual slow down, and completed conversion after 3 hours. The results indicate that the higher the content of acrylate groups in black seed oil, the faster the thermal crosslinking reaction occurs [11, 13]. As the acrylate group content increases, the density of acrylate groups in the crosslinking system also increases, leading to an increase in the rate of acrylate group conversion.

The transformation of the gel fraction and swelling degree of the research samples with different levels of acrylate-functionalized groups during the cross-linking process at 40°C is presented in Fig. 9.

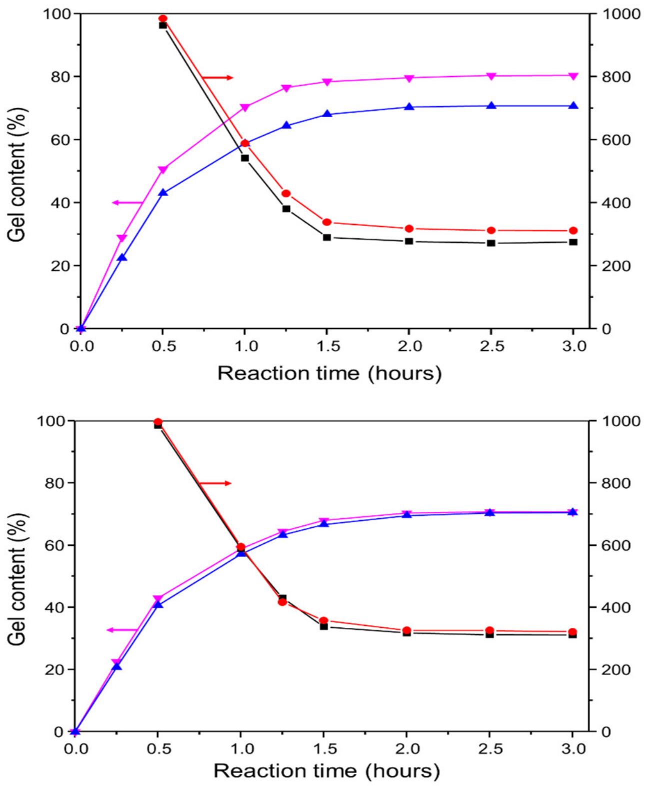


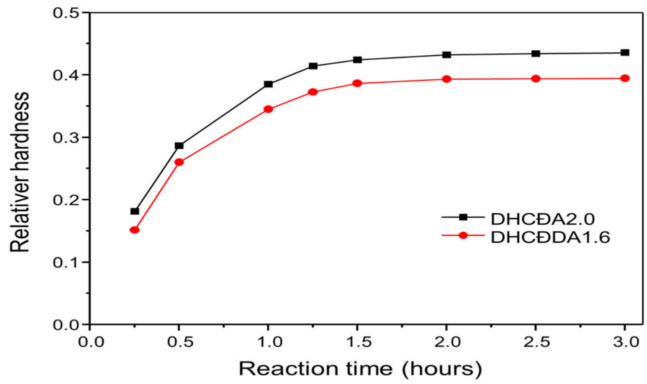
Figure 9. Changes in gel content and swelling ratio of the studied samples with different levels of acrylate group content of black seed oil during the crosslinking process at 40°C

Fig. 9 illustrates that initially, both crosslinking systems DHCĐA2.0/D.D.1173 and DHCĐA1.6/D.D.1173 completely dissolve in chloroform, indicating a gel content of 0%. However, after 1 hour of reaction, the gel content of the DHCĐA2.0/D.D.1173 system rapidly increases to 70.4%, and the DHCĐA1.6/D.D.1173 system increases to 58.8%. This result is consistent with the transformation of acrylate groups during the reaction. Subsequently, the gel content increases slowly, and after 3 hours of reaction, the gel content of the DHCĐA2.0/D.D.1173 system reaches 80.4%, and the DHCĐA1.6/D.D.1173 system reaches 70.7%. The changes in swelling ratio of these coatings also follow a corresponding pattern. After 3 hours of reaction, the swelling ratio of the DHCĐA2.0/D.D.1173 system gradually decreases from 962% to 275%, and the DHCĐA1.6/D.D.1173 system decreases from 984% to 311%. Thus, after 3 hours of reaction, the crosslinked systems at ambient temperature based on acrylated black seed oil have undergone crosslinking, solidifying to form a tightly crosslinked three-dimensional network. The coatings become solid and rigid.

The changes in gel content and swelling ratio of the DHCĐA1.6/D.D.1173 and DHCĐMA1.6/D.D.1173 systems during the crosslinking process at 40°C are presented in Fig. 10.

Observing from Fig. 10, the changes in gel content and swelling ratio of the DHCĐA1.6/D.1173 and DHCĐMA1.6/D.1173 systems follow a similar pattern: rapid increase in gel content and rapid decrease in swelling ratio after 1 hour of reaction, followed by slow and almost constant changes in gel content and swelling ratio after 3 hours of reaction. Both systems have the same acrylate group content of 1.6 mol per unit mass of oil molecule but possess different acrylate nature. Despite the differences in the gel content and swelling ratio between the two systems, the variation is not significant. This can be attributed to the spatial effect of the methyl group in the DHCĐMA1.6/D.1173 system, which reduces the flexibility of the molecules.

From Fig. 10, it can be observed that the DHCĐA2.0/D.1173, DHCĐA1.6/D.1173, and DHCĐMA1.6/D.1173 crosslinking systems exhibit rapid increases in relative hardness after 1 hour of reaction, reaching values of 0.387, 0.345, and 0.337, respectively. Subsequently, the increase slows down, and the values remain unchanged after 3 hours of reaction, reaching values of 0.46, 0.39, and 0.39, respectively. The changes in relative hardness of the samples correspond well with the content and variations of acrylate groups during the reaction at 40°C in the studied systems.



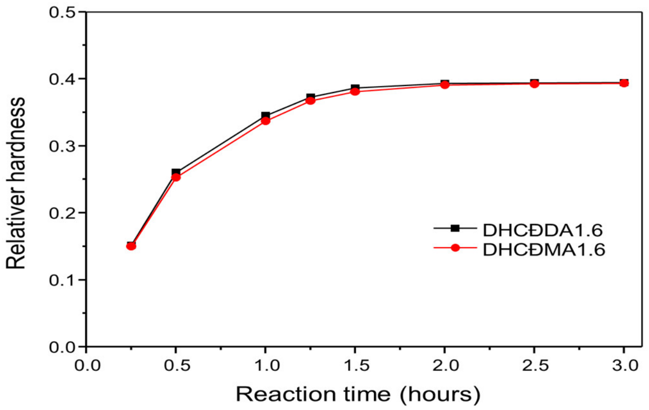


Figure 10. Changes in the relative hardness of the DHCĐA2.0/D.1173, DHCĐA1.6/D.1173, and DHCĐMA1.6/D.1173 crosslinking systems during the crosslinking process at 40°C

4. CONCLUSION

The thermal crosslinking reaction of acrylated black seed oil occurs rapidly at 40°C for 3 hours in the presence of initiator D.1173, resulting in a tighter crosslink compared to systems using initiators PI.PB, TPO, I.184, PI.907, and D.1173. The activity of the initiators for acrylated black seed oil system with 3% content is arranged in the order of D.1173 > PI.907 > I.184 > TPO > PI.PB. Initiator D.1173 is selected as the initiator for the thermal crosslinking reaction of acrylated black seed oil.

The acrylate group content significantly influences the crosslinking reaction, as well as the processability and properties of the coating. A content of 2.0mol acrylate/mol molecular weight results in rapid acrylate group conversion, co mpleted after 3 hours of reaction, yielding coatings with good physical properties on glass and CT3 steel substrates.

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THÔNG TIN TÁC GIẢ

Đàm Xuân Thắng

Khoa Công nghệ Hóa, Trường Đại học Công nghiệp Hà Nội