دراسة وتقييم الخواص الحرارية للشبكات البوليميرية المتداخلة من الايزوسيانات TDIوالبولي أول مع راتنج البوليستر الغير مشبع

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الملخص:-

تمت دراسة تأثير اضافة راتنج البوليستر الغير مشبع UPE الى الخليط البوليميري المتكون من (بولي اول – ايزوسيانات TDI). واستنتج الباحثون الى ان اضافة نسبة مختلفة من الراتنج الى الخليط البوليمري (TDI–polyol) يحسن من الخواص الحرارية (التوصيل الحراري والحرارة النوعية). تم تحضير خمس عينات من الخليط لبيوليمري المتداخل بنسب مئوية كالتالي % (٤٠،٣٠،٢٠،١٠). لاحظ الباحثون في هذه الدراسة انه عند تقليل نسبة البولي اول في الخليط البوليمري تنخفض الحرارة النوعية كما يوضح الشكل (١) ذلك، ولاحظ ايضا زيادة في الموصلية الحرارية عند اضافة راتنج البوليستر الغير مشبع الى الخليط البوليمري المتكون من (١٢,٥ polyol–87.5TDI) حيث وجدو ان الموصلية الحرارية تزداد مع زيادة اضافة راتنج البوليستر الغير مشبع بنسب مئوية% (٤٠،٣٠،٢٠،١٠،٠) والموصلية الحرارية كالاتي (٠,١٦٨،٠,١٦٢،٠,١٥٦،٠,١٤٩،٠,١٢٢) واط/م.س°. لاحظ الباحثون ان مقدار الموصلية الحرارية يقل في الخليط البوليمري المتداخل عند نسبة بولي اول % ٢٠ اي (٢٠%polyol–80%TDI) عند نسبة اضافة راتنج البوليستر الغير مشبع % ٢٠ وهي ٠,١٠٤ واط/م.س وعند انخفاض الموصلية الحرارية يزداد العزل الحراري لهذا البوليمر الشبكي المتداخل وهذه النسبة تعتبر افضل نسبة توصل اليها الباحثون لصنع طلاء بوليميري يستخدم في العزل الحراري.

Keys words :Polyol ،unsaturated polyester resin, toluene diisocyanate ،Specific heat ، Thermal conductivity

Study and evaluation thermal properties of IPN's TDI and polyols with unsaturated polyester resins

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Abstract

The effect of adding unsaturated polyester resin on the polyol-TDI was studied. The researchers concluded that adding different proportions of the resin to the polyol-TDI improves the thermal properties (thermal conductivity - specific heat). The five samples were prepared by add percentage of unsaturated polyester resin to (polyol-TDI) blends (10%, 20%, 30%, and 40%), in this study, it was observed that when reducing the percentage of polyol in IPNS polymer , the specific heat decreases as Figure (1) illustrates that. An increase in thermal conductivity was found when adding unsaturated polyester resin to the polymeric mixture (polyol-TDI), at polyol percentage 12.5%, it has been observed that the thermal conductivity of the polymeric mixture (polyol-TDI) increases with the increase in the percentage of unsaturated polyester resin (0,10,20,30,40)%(0.122, 0.149, 0.156, 0.162, 0.168) W/m.°C, respectively. While the thermal conductivity in the polymeric mixture consisting of (20%polyol-80%TDI) decreases when adding 20% of the unsaturated polyester resin to 0.104 W/m.°C and thus we obtain a polymeric coating with thermal insulation properties at this ratio.

Introduction

Interpenetrating polymer networks (IPNs) are defined as the combination of two or more polymer networks which are interlaced on a polymer scale. [1] Unlike other kinds of methods such as physical blending, chemical grafting, or crosslinking, the polymer networks in IPNs do not covalently bond to each other, they simply entangle in such a way that they are concatenated and cannot be pulled apart. IPNs might be formed in a simultaneous or sequential manner with all the polymer chains form infinite intertwined networks or at least one or more polymers are cross-linked and others are linear or branched (so called semi-IPN). [2] The compatibility of two or more otherwise immiscible polymers is greatly enhanced through the formation of IPNs. The minimum performance of coating systems can be improved upon exposure and aging by introducing the polymer network structure (IPNs) [3]. These networks can be defined as groups of chemically different polymers, where polymer chains are completely intertwined with each other. Thus, IPN is a mechanism by which different chemically incompatible polymers can be incorporated. As the bonding density of polymeric IPNs increases, wet vapor transport (MVTR) rates decrease linearly. Further their high crosslink density and low MVTR values, IPN properties can be various to meet specific purposes by changing the composition of constituent polymers and other factors. IPNs can replace a multi-layer coating system that provides the same level of technical characteristics and durability. The modified IPN coating material enhances thermal stability, impact behavior and water-like properties compared to those obtained from blending technology. The technology interpenetrating the polymer network as a coating material at present in the case of appearance with limited literature [4]. In 2004, A. Anandprabu and M. Alagan [5], the studied [Mechanical and thermal studies of intercross-linked networks based on silicon zed polyurethane-epoxy/unsaturated polyester coatings, the result, mechanical properties were enhanced with incorporation of PU (10 wt. %) and silicone (10 wt. %) due to the toughening of brittle epoxy and

UP systems. The introduction of PU into unmodified epoxy/UP coating systems reduces the thermal stability due to the presence of thermally weak urethane linkages whereas, the incorporation of 10 wt.% silicone into PU modified epoxy/UP systems improves their thermal stability due to the partial ionic nature, high bond energy and thermal stability of –Si–O–Si– linkage. in 2013, Majeed *et al.*, [6] studied the Enhancing thermal and Water absorption properties of unsaturated polyester and epoxy by Nano carbon black (N220) Powder. The weight fraction of carbon black (1, 2, 4, 6, 8, 10 wt. %) with epoxy resin and polyester. the results of thermal conductivity have increased for epoxy nanocomposite, and unsaturated polyester at 10 wt.% while the water absorption decrease for unsaturated polyester and epoxy nanocomposite at 4 wt.% and 6 wt.%, respectively In (2017), A. Raad., et al., [7] Experimental Study for Some of the Mechanical and Physical Properties for the Binary Polymer of (Epoxy resin – Polyurethane, The result show that the Impact testing and tensile test increase submerging duration (0−28) day for samples, as for the tests of hardness, bending and compression decreased by increasing the submerging duration of the samples, while the thermal conductivity increases by increasing the submerging duration of the samples. . in 2018, H. Khalaf *et al.*, [8] studied the Thermal conductivity and diffusion coefficient of polymer blend 80%EP/20%UPE reinforced with sand particles The polymer blend was enhanced as obtained by adding sand particles of particle size (53 µm) with different weight fractions (5, 10, 15, 20%), The results showed that the addition of sand powder to the blend (80% EP / 20% UPE) will increased thermal conductivity, with optimum / minimum diffusion coefficient of (HCl) / (NaOH), respectively. in 2019, [9] A. El Bouari and et al., the studied Alfa fiber−polyurethane composite as a thermal and acoustic insulation material for building applications, Thermal conductivity, mechanical properties and acoustical performances of composites were investigated as a function of fibre content. In this study the aims of the search are:

- Effect of polyol on the Toluene Diisocyanate TDI of polymeric coatings used.
- Effect of adding unsaturated polyester resin on polymeric mixture (polyol-toluene diisocyanate) in polymeric coatings.
- Studying the thermal properties of the produced coating and finding better results.

Material experiment

Unsaturated Polyester Resin

Unsaturated polyester resins are one of the most widely used thermosetting materials in the coatings and composites industry [10], which was supplied from Saudi industrial resin CO. LTD, P. O. Box 7764, Jeddah 21472, Kingdom of Saudi Arabia.

Polyol

The polyols were provided by the DOW Chemical Company, in this work, it was used polyol of the type polyether polyol where 90% of polyols are used in the manufacture of flexible polyurethane. Isocyanate was provided by the DOW Chemical Company [11].

Preparation technique

Hand lay-up molding was used in the process of preparation of the samples under test and thus samples were prepared as follows:

Study the thermal properties of add unsaturated polyester resin to the mixture (polyol-isocyanate).

The five samples were prepared by added five percentage of (polyol-toluene diisocyanate) mixture unsaturated polyester resin to (polyol-TDI) blends (10%, 20%, 30%, and 40%). The unsaturated polyester resin is put in different proportions to the polyol in a plastic container and after mixing well for two minutes at room temperature (25-30) C and then put the toluene as a solvent for the mixture that blends, Toluene addition ratio should be equal to (polyol-isocyanate) mixture, The polymer blends are then mixed thoroughly for a minute. Mix the mixture in a plastic container, a hand lay-up molding was used in process preparing the samples. Finally, isocyanate and MEKP are added to the polymeric blend. The samples are then poured into heat resistant plastic plates resulting from the polymerase reaction. The samples are then left to solidify for 24 hours.

The following tables show the percentages of adding unsaturated polyester resin to (polyol-isocyanate) mixture; the percentages of polyols are (12.5%, 20% and 50%).

Toluene mL	Toluene diisocyanate %	Polyol %	Polyester %
100	87.5	12.5	0
100	78	12	10
100	70	10	20
100	61.25	8.75	30
100	52.5	7.5	40

Table (1) showing the percentage of unsaturated polyester added to (polyol−toluene diisocyanate) mixture with a percentage of polyol 12.5 % (PU 1:8)

Toluene mL	Toluene diisocyanate %	Polyol %	Polyester %
100	80	20	0
100	72	18	10
100	64	16	20
100	56	14	30
100	48	12	40

Table (2) showing the percentage of unsaturated polyester added to (polyol−TDI) mixture with a percentage of polyol 20 % (PU 1:5).

Toluene mL	TDI %	Polyol %	Polyester %
100	50	50	0
100	45	45	10
100	40	40	20
100	35	35	30
100	30	30	40

Table (3.6) showing the percentage of unsaturated polyester added to (polyol−isocyanate) mixture with a percentage of polyol 50 % (PU 1:1).

Result and Discussion

Specific heat of IPNS Polymer

In general, Figure (1) shows the specific heat behavior of the polymeric materials under study, Specific heat values increase with increasing temperature. Specific heat increases almost linearly as the temperature rises down to the degree of glass transition, Specific heat then rises abruptly and then the specific heat continues to rise gradually down to the Max value of the specific heat, which is proportional to 3R each atom. The results found in the study now are agree with those of amorphous polymers, Specific heat change with overheating can be explained by Tarasov's theor. This assumed that polymeric materials consist of layers of atoms that are strongly bonded by major covalent bonds; the overlap between chains or layers is due to weak, Van der Waals bonds.

Figure (1) shows the behavior (Cp-T) of this polymeric coating in the temperature range (323-873) K, when the addition of 50% polyol the specific heat value of this polymeric coating is high relative to the rest of the samples.

This can be explained in order to contain the composition of the polymeric rigid groups represented by aromatic rings as a polyol contains benzene rings and when the increase of polyol, the heat capacity is high and up to 65J/mol.K, thus increasing the of cross-link density in this type of thermosetting polymers.

And show figure (1), when adding 20% of the polyol to the polymeric composition, we notice that the specific heat rise but less than 50% of the polyol, When reducing the percentage of polyol to 12.5%, the specific heat decreases less than the percentage of polyol 20% and 50% When reducing polyol, the specific heat decreases due to the increased intensity of the entanglement and therefore the molecular weight increases with higher cohesion energy and constrains molecules and chains and decreases in degrees of freedom responsible for specific heat The sequence caused a decrease in the specific heat content of polymeric coatings at 20% and 12.5% of polyol in the presence of the synaptic agent of unsaturated polyester resin.

It is noted from the curve (Cp–T) that the specific heat value of the three polymeric coatings that they rise when the addition of unsaturated polyester resin and this behavior is expected to occurs because the resin contain on the aliphatic groups Which increases the degrees of freedom to vibration with the rise of temperature, which is responsible for the value of specific heat We conclude from the nature of the curve (Cp–T) that the specific heat rises linearly with the temperature as a result of increasing molecular movement and continue to rise the specific heat down to the value of the charcoal

This is consistent with the IPN's Polymers concept that it is not a mixture of two substances but rather a complex polymeric composition. It is clear from the above that this variation in the values of specific heat between the models under study is due to many factors that affect the behavior of specific heat with temperature change, including the chemical composition of the polymer and molecular weight and complex composition of interfering polymeric blend (IPN's polymers). The specific heat values of the polymeric mixture follow the following thermal gradient:

IPN at 50%PO.>IPN at 20%PO.>IPN at 12.5%PO.

Thermal conductivity

Heat conduction can take place only when bodies at different temperatures are in physical contact. The heat flow will be from the body at the higher to the body at the lower temperature. In solids, heat is transferred from one location to another depending on the mechanism of conduction by electrons, photons, or both, depending on the type of solids we are dealing with. In conducting materials, free electrons are responsible for the transfer of thermal energy as well as phonons. In heat-insulating materials, heat is transmitted by phonons [12, 13]. Figure (2) shows the results of thermal conductivity of pure polymeric mixture (12.5% polyol–87.5% toluene diisocyanate) is 0.122 and when the addition of unsaturated polyester resin in different proportions as (10, 20, 30 and 40) % we note the increase of thermal conductivity values (0.149, 0.156, 0.162

and 0.168) W/Kg.C respectively. This is because the addition of the resin to the polymeric composition (polyol–toluene diisocyanate) leads to a reduction in the pores of the polymeric material (PU 1: 8) and therefore increases the vibrations in the internal polymer structure of the resin, which increases with increasing temperature. These results agree with the results obtained by M. Khan and A. Balandin [14] and Chinua Shiu *et al.*, [15].

Figure (3) shows the variation of the thermal conductivity values of the polymeric mixture (20% polyol–80% toluene diisocyanate) when adding unsaturated polyester resin to Polymeric composition, this variation in thermal conductivity values is due to the heterogeneous distribution of unsaturated polyester resin within the polymeric composition, as shown in table (4.17). The decrease in thermal conductivity values when the resin is added to the polymer mixture (20% polyol–80% toluene diisocyanate) is due to an increase in the crosslink agent due to the restriction of polymer chains and structural units and to the obstruction of lattice vibrations.

Figure (1): represents the specific heat of polymeric coatings consisting of a (polyol–toluene diisocyanate) mixture after the addition of unsaturated polyester resin, when the polyol ratio is (12.5, 20 and 50) %.

Table (4): showing percentages of unsaturated polyester resin added to the polymeric mixture (12.5 % polyol–87.5 %toluene diisocyanate) and its effect on the thermal conductivity of the formed for polymeric coatings.

					Unsaturated

40 %	30 %	20 %	10 %	0 %	Polyester (Wt. %)
0.168	0.162	0.156	0.149	0.122	Thermal Conductivity w/m.°c

Figure (2) shows the variation of the thermal conductivity values of the polymeric mixture (12.5% polyol−87.5% toluene diisocyanate) when adding unsaturated polyester resin to Polymeric composition.

Table (5): showing percentages of unsaturated polyester resin added to the polymeric mixture (20 % polyol−80 %toluene diisocyanate) and its effect on the thermal conductivity of the formed for polymeric coatings.

40 %	30 %	20 %	10 %	0 %	Unsaturated Polyester (Wt. %)
0.159	0.119	0.104	0.118	0.181	Thermal Conductivity w/m.°C

Figure (3): shows the variation of the thermal conductivity values of the polymeric mixture (20% polyol-80% toluene diisocyanate) when adding unsaturated polyester resin to Polymeric composition.

Conclusion

- Polyurethane with unsaturated polyester resin can be used as polymeric mixtures to produce heat-insulating dyes and control their physical properties

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