

CHEMICAL WELDING OF POLYURETHANES AND THEIR COMPOSITES

ХІМІЧНЕ ЗВАРЮВАННЯ ПОЛІУРЕТАНІВ І КОМПЗИТИВ НА ЇХ ОСНОВІ

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Chemical welding as an attractive alternative to classical joining techniques occurs through the formation of new chemical bonds between neighboring molecules at the contacting surfaces to be joined. This review paper presents the current state of the chemical welding of polyurethanes and their composites via dynamic covalent bonds. The strength of welded joints obtained by different welding technologies was compared. Different processing parameters affecting the joint quality, namely welding time and welding temperature were summarized. The future perspectives of chemical welding of polyurethanes and their composites were discussed in the paper. 12 Ref., 7 Fig.

Хімічне зварювання як альтернатива класичним методам з'єднання базується на утворенні хімічних зв'язків між функціональними групами контактуючих поверхонь. У представленій оглядовій роботі проаналізовано сучасний стан хімічного зварювання поліуретанів завдяки наявності в їх структурі динамічних ковалентних зв'язків. Встановлено, що якість зварних з'єднань залежить від параметрів зварювання, пов'язаних із технологією зварювання. Основними параметрами, що визначають міцність зварних з'єднань, є температура зварювання та тривалість зварювання, тоді як контактні зусилля стиску при зварюванні лише незначним чином впливають на міцність. Міцність зварних з'єднань, як правило, зростає зі збільшенням температури або тривалості зварювання. Якість одержаних зварних з'єднань контролюється руйнівними та неруйнівними способами контролю. Важливо зазначити, що застосування хімічного зварювання не обмежується плівковими матеріалами і використовується також для зварювання деталей великих товщин. Встановлено, що хімічне зварювання застосовується і для композитів на основі поліуретанів, які привертають велику увагу завдяки своїм гібридним властивостям. Більш того, проведення хімічного зварювання композитів можливе з використанням світлового випромінювання, що пов'язано з присутністю світлочутливих наповнювачів, які каталізують хімічні реакції між функціональними групами на контактуючих поверхнях. Оскільки керування світлом відбувається дистанційно, локально та тимчасово, існує можливість проведення зварювання без впливу на навколишні ділянки матеріалу. У статті представлено порівняння міцності зварних з'єднань композитів, одержаних за різними технологіями зварювання. Встановлено, що утворення хімічних зв'язків між функціональними групами контактуючих поверхонь під дією випромінювання в ближній інфрачервоній області відбувається з вищою швидкістю і 1 хв достатньо для утворення якісного з'єднання. Бібліогр. 12, рис. 7

Keywords: polyurethanes, composites, chemical welding.

Ключові слова: поліуретани, композити, хімічне зварювання

Introduction.

Polymeric materials have been widely used in various fields of advanced technology, including transport, defense, civil industries due to low weight, specific stiffness, corrosion resistance, and high fatigue life. In advanced technologies, manufacturing large parts requires a complex mold, which consequently means a substantial increase in the cost. However, such a complex part can be manufactured through the assembling of small parts by using different joining techniques. Thus, there is a growing need for a fast and effective way of joining polymer structures.

Welding technology serving as an exceedingly good tactic to save materials and provide an excellent

bonding strength in the field of metal processing is also extensively applied in thermoplastic polymer materials. High-quality welding could be obtained when thermoplastic polymers are heated to their viscous flow state in the contact area. Thermosetting polymers are quite advantageous in comparison to thermoplastics since they have higher thermal stability, fixation ability, and can perform higher levels of mechanical work. Moreover, they cannot be replaced by thermoplastics in a wide range of engineering applications, especially those requiring high-performance such as the aircraft and automotive industry. However, due to the permanent molecular structure, thermosets could not melt or be dissolved once synthesized.

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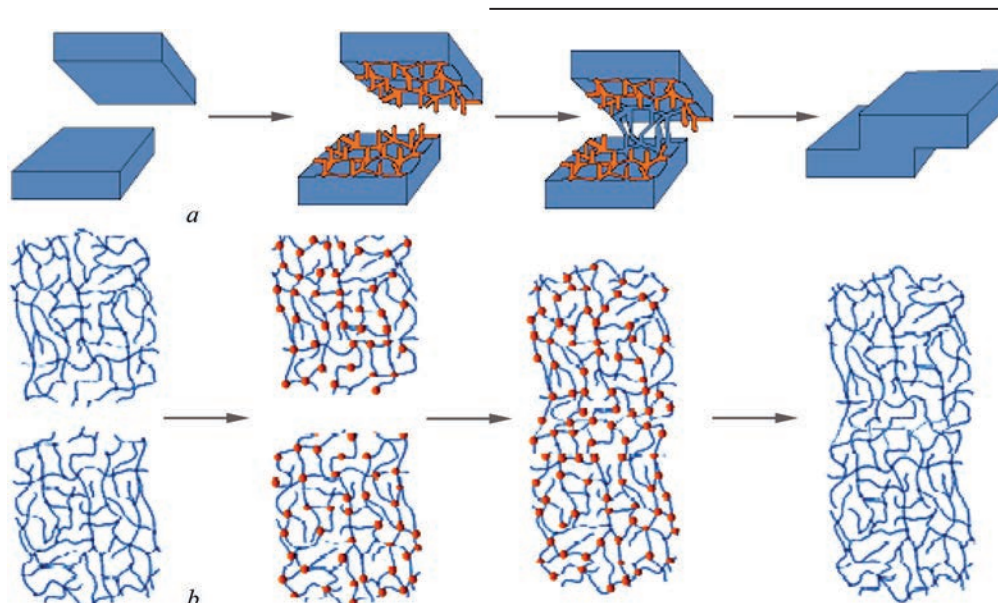


Fig. 1. Chemical welding of two surfaces involves chemical reactions (a). Topological rearrangements occur via exchange reactions on a macromolecular chain during chemical welding (b).

Рис. 1. Хімічне зварювання двох поверхонь внаслідок перебігу хімічних реакцій (a). Топологічні перетворення, які відбуваються внаслідок перебігу реакцій обміну на макромолекулярних ланцюгах під час хімічного зварювання (b).

As a consequence, the traditional diffusion welding technology cannot be simply applied to thermosets and their composites. Therefore, thermoset systems must rely on chemical welding only to join them.

Chemical welding refers to the process that occurred through the formation of new chemical bonds between neighboring molecules at the contacting polymer surfaces to be joined. In particular, vitrimers as a new class of polymers can rearrange their network topology via thermally triggered bond exchange reactions (BERs) at elevated temperatures without affecting the average crosslinking degree. Thus, when two separated vitrimer surfaces are brought into contact the reversible associations (bridges) are formed across the interface resulting in chemical welding (Fig.1). Polyurethanes represent a class of materials with important industrial applications that exhibit favorable mechanical, physical, and biocompatible properties [1 – 3]. Moreover, vitrimeric characteristics of polyurethanes have been already reported [4 – 5]. This review paper summarizes results on investigations of the current state of the chemical welding of polyurethanes and their composites.

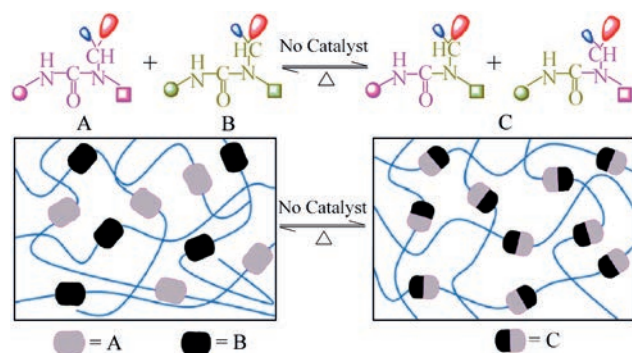


Fig. 2. Thermal-triggered mechanism of dynamic hindered urea bonds exchange [6].

Рис. 2. Механізм обміну карбамідними зв'язками [6].

Recent work on chemical welding.

Recently, to tackle the obstacle the vitrimer polyurethanes have been easily synthesized by using the designed secondary amine (through the addition reaction of aziridines and lauric acid) and isophorone diisocyanate in the absence of any catalyst [6]. The long strip of the sample with a width of 4 mm and thickness of 2 mm was cut in half with a razor blade and then the two pieces were put together at 25 °C for 3 min, followed by welding at 120 °C for 60 min without external stress. The thermal-triggered mechanism of chemical welding via dynamic hindered urea bonds exchange under catalyst-free conditions is shown in Fig. 2. It was found, that the welded joint can be stretched up to 200 % strain without tearing and can lift a weight of 0.5 kg without breaking at the welded part (Fig. 3).

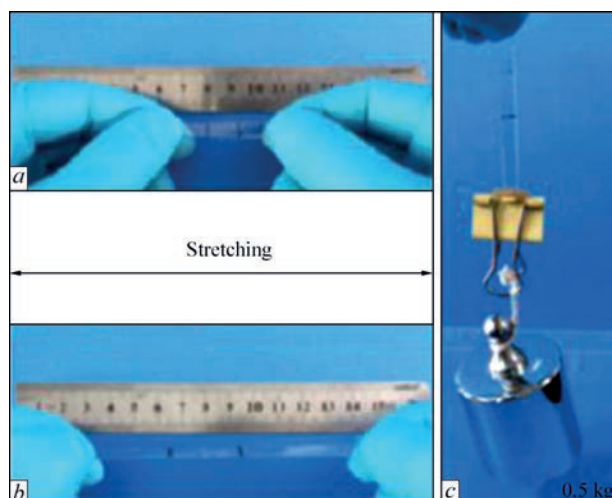


Fig. 3. Photograph of film welded at 120 °C for 60 min before (a) and after (b) stretching. Photograph of welded joint with a 0,5 kg weight lifting test (c) [6].

Рис. 3. Фотографії зварних з'єднань, одержаних за 120 °C протягом 60 хв до (a) та після розтягування (b). Фотографія випробування зварного з'єднання на підняття ваги в 0,5 кг (c) [6].

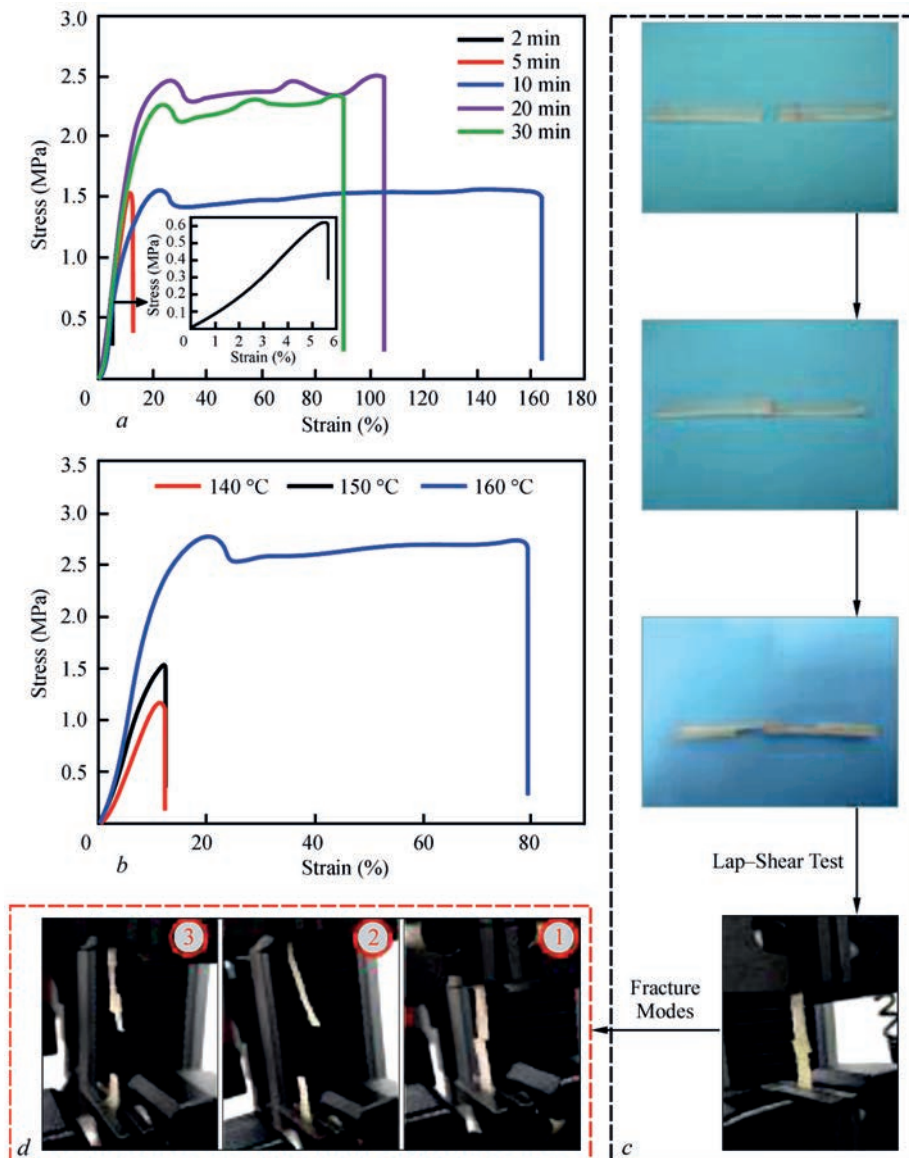


Fig. 4. The mechanical properties of the welded joint at 150 °C at different times (a) and different temperatures for 5 min (b). Specimen of the lap-shear test (c). Fracture modes of the welded joints (d) [7].

Рис. 4. Діаграма деформування зварних з'єднань, одержаних за 150 °C протягом різного часу зварювання (a) та за різних температур протягом 5 хв зварювання (b). Підготовка експериментальних зразків внакладку до випробування на зсув (c). Різні види руйнування зварних зразків (d) [7].

In recent years with increasing attention on the environment and economy, various low-cost and sustainable bio-based resources have been used as alternatives to petroleum-based materials. Fully biobased and recyclable polyurethane-vitrimers were designed via classical polyurethane chemistry: reaction of polyethylene glycol, castor oil, and hexamethylene diisocyanate, using dibutyltin dilaurate and ethyl acetate as catalyst and solvent, respectively [7]. The chemical welding through transcaramoylation reaction of carbamate bonds was carried out (i) at 150 °C for different time (2 min, 5 min, 10 min, 20 min, 30 min) and (ii) at different temperature (140 °C, 150 °C, 160 °C) for 5 min by keeping the other parameters constant. This study showed that the stress of chemically welded joints tended to increase with welding time at a fixed temperature (Fig. 4a). It is worth not-

ing that the welded joints with welding time of 2 min, 5 min (Fig. 4d¹), and 10 min (Fig. 4d²) all broke at the overlapped part and had relatively lower stress at break. However, the welded joints under the same temperature but with a longer welding time (20 min and 30 min) had stress at break higher than 2 MPa and broke at bulk material instead of the overlapped part (Fig. 4d³) due to nearly complete transcaramoylation reaction at the overlapped part. Welding temperature also plays an important role in weld quality. It can be seen in Fig. 4b that higher welding temperature promoted better recovery of the material strength across the interface with the same welding time. Importantly, samples chemically welded at 140 °C (Fig. 4d¹) or 150 °C (Fig. 4d²) were broken at the overlapped part and had relatively lower stress at the break, whereas the samples welded at 160 °C

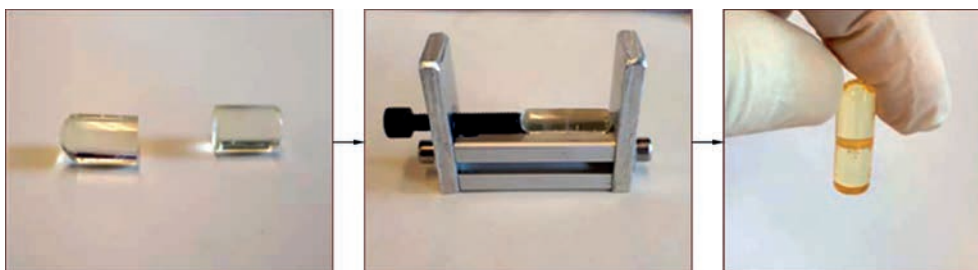


Fig. 5. Visual demonstration of chemical welding of poly(thiourethane) vitrimer films at 180 °C for 40 min under pressure [8].

Рис. 5. Демонстрація хімічного зварювання полі(тіоуретанової) вітримерної плівки за 180 °C під тиском протягом 40 хв [8].

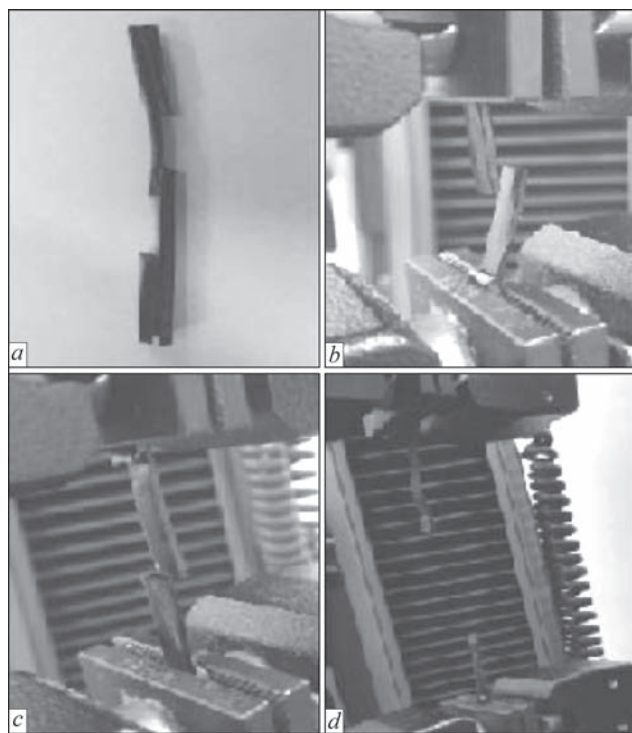


Fig. 6. The sample of the lap-shear test (a). The photographs of the lap-shear test from the samples with different weld times: 2 min (b), 5 min (c), and 20 min (d) [12].

Рис. 6. Зварне з'єднання для тесту на зсув внахлост (a). Фотографії випробування на зсув внахлост з'єднань, одержаних за різного часу зварювання: 2 хв (b), 5 хв (c), 20 хв (d) [12].

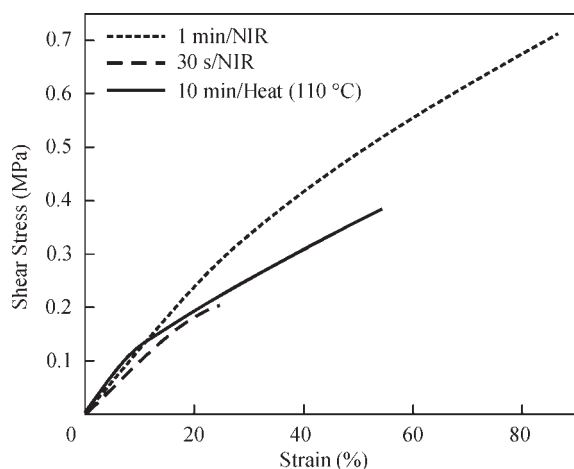


Fig. 7. Comparison of welding effects of CNTs-polyurethane vitrimer nanocomposite induced by NIR and heat [12].

Рис. 7. Діаграми деформування зварних з'єднань нанокмполімерів, одержаних під дією випромінювання в ближній інфрачервоній області та тепла [12].

were broken at bulk material part (Fig. 4d³). Thus, a facile strategy to select and optimize the processing conditions for chemical welding of films based on polyurethanes could be realized through changes in welding time and welding temperature.

The welding process is not limited to the film joints, and the thick samples can be chemically welded. Thus, a new type of vitrimers were prepared from commercially available monomers (trimethylolpropane tris(3-mercaptopropionate), hexamethylene diisocyanate) by an easy procedure using tert-butyl isocyanate and dibutyltin dilaurate as the catalysts [8]. The synthetic reaction has click characteristics, which assure a great homogeneity of the poly(thiourethane) network structure. These materials can be chemically welded at 180 °C for 40 min under pressure, as it is shown in Fig. 5. The trans-thiocarbonylation reaction, which has a non-dissociative mechanism, responsible for the welding ability of these vitrimers has been chemically assessed by the use of model compounds and gas chromatography coupled to mass spectrometry. The non-dissociative character of the trans-thiocarbonylation process has been confirmed in the materials by FTIR spectroscopy.

In the above studies, the heating stimulus was utilized to activate the chemical welding. However, direct heating is unsuited for a heat-sensitive application like biomedicine, and it is also limited when the targeted locations could not be reachable in some special engineering environments. In comparison with heating, the near-infrared (NIR) light-responsive method possesses many distinctive advantages including (i) remote activation is available due to the travel characteristics of light; (ii) regional activation can be realized by regulating the spot size without intervening with the surrounding environment; (iii) light stimulus is immediate by turning the light source on or off [9]. A common approach to creating light-responsive chemical welding is to introduce photothermal fillers, such as metal nanoparticles, conjugated polymers, rare earth organic complexes, carbon nanomaterials, photothermal fillers. Among them, carbon nanotubes (CNTs) as novel 1D nanomaterials have many excellent performances, namely high mechanical properties, electrical and thermal conductivity. Most important of all, CNTs can absorb NIR light and generate a large amount of heat [10 – 11]. Therefore, the addition of CNTs to polyurethane-vitrimers may be a good option to carry out chemical welding induced by NIR light.

Recently, CNTs-polyurethane vitrimer nanocomposites were synthesized by chemical reaction of the hexamethylene diisocyanate with polyethylene glycol ($M_n = 2000$) and castor oil in the presence of dibutyltin dilaurate as a catalyst for transcarbamoylation, with different content of CNTs ranging from 0 to 1 wt.% [12]. Chemical welding of the nanocomposites induced by NIR light (980 nm) was conducted with an overlap area of 1.0 mm×1.0 mm and irradiation by a NIR light at different times. The light intensity of the NIR laser irradiation was 1.41 W cm⁻². Although the shortest welding time was only 0.5 min, the shear strength has already reached 0.2 MPa, which was an amazing welding efficiency. As seen in Fig. 6b-d, the shear strengths of the welded joints gradually increased with the extension of welding time from 2 min to 20 min proving that longer welding time enhances the welding effect. Beyond that, the effect of CNTs content on the welding efficiency was discussed as well. It was found that the composite with 0.5 wt.% CNTs has a higher thermal conductivity than that with 0.05 and 0.1 wt.% CNTs under the same welding conditions, which promotes transcarbamoylation and endows the sample with excellent welding performance.

Recently, the chemical welding of the nanocomposites induced by heat and NIR light was discussed separately, and the welding efficiency of the two methods was compared (Fig. 7) [12]. It was found, that the two pieces of CNTs-polyurethane nanocomposites can never be chemically welded at 80 °C ($T_v = 90$ °C) due to the lack of adequate exchange reaction at this temperature. However, the specimens could be welded together at 110 °C for 10 min. It should be noted, that temperature of nanocomposites produced by the photothermal effect of CNTs has reached 90 °C 0.5 min or 110 °C at 1 min. It was surprising to find that the shear strength of the sample irradiated for 1 min by NIR was much stronger than that of the specimen heated at 110 °C for 10 min, which further proves that the NIR-welding technology possesses a higher efficiency. According to these results, chemical welding induced by NIR light would be beneficial for joining or repairing the CNTs-polyurethane nanocomposites.

Conclusions.

Chemical welding is a relatively new welding approach that opens the way towards assembly of polyurethane materials without adhesives or molds. Thus, polyurethanes can be facilely welded by heat. The weld quality could be controlled by different welding parameters associated with the welding procedure such as welding time and welding temperature. Chemical welding of polyurethane nanocomposites could be induced by heat and NIR-light. The NIR-induced welding technology is not only convenient but also environmentally friendly and has higher efficiency compared with thermal technology. Moreover, the

NIR-induced welding technology makes remote and spatial welding technology of nanocomposites possible. Although significant progress was made by researchers in the past years, their inputs are mostly based on observation of the weld with electron microscopic techniques and test data coming from mechanical tests. Work is left to be done to get high joining strengths with a reasonable welding time to enable the efficient transfer of new technologies to the industry in the close future.

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