Preparation and Properties of PU/MOF-199 Nanocomposite Coated Polyester Fabric

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Abstract

Polyurethanes (PUs) are most versatile group of industrially important polymers in today's world. It has applications in various fields like, coatings, paints, foams, elastomers, and adhesives. Because of the excellent properties, its industrial applications as a coating are increasing every day. Also it is possible to get tailor made properties from PU. Over the past 10 years, developments in bio and physical chemistry, microscopy, and engineering have shown great strides in understanding the properties and developing applications for nanoparticles. These technological innovations have led to the development of many tiny structures such as nanoshells, nanospheres, nanotubes, nanofillers, and metal organic frameworks. There are many commercial products available today using these nanomaterials including transparent sunscreens, stain-resistant clothing, coatings, self-cleaning glass, paints, sports equipment, and numerous applications in electronics. Nanofillers have previously been incorporated into paints and coatings to increase their mechanical strength, thereby increasing their lifespan. However, dirt and bacteria stil accumulate on almost every surface, causing significant problems for cleaning and maintenance of these surfaces. Although these surfaces can be cleaned using chemical detergents accompanied with scrubbing and sometimes a high-pressure water jet, all these processes have inherent deficiencies such as the use of chemical detergents and high energy/labour costs.

In this study, we have investigated the water vapor permeability of polyurethane/metal organic framework-199 (PU/MOF-199) nanocomposite coated polyester fabrics. MOF-199 was synthesized by solvo-thermal method at room temperature. First, the mixtures of PU/MOF-199 nanocomposites with different MOF-199 contents were prepared in dimethyl formamid as a solvent and coated on polyester fabric using transfer coating method. Then, different mechanical tests such as tensile strength, tear strength, accelerated life, water penetration and water vapor permeability tests were performed. Furthermore, it appears that the water vapor permeability of fabric is decreased with increasing amount of MOF-199 except 1 wt.% of MOF-199. It has also been noticed that mechanical characteristics and life cycle of the coated fabric with MOF-199 increased slightly in comparison to the neat polyurethane coated fabric.

Key words: Polyurethane, MOF-199, Coated Fabric, Water Vapor Permeability, Breathability

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1. Introduction

Polyurethane is an important group of products within the family of polymers. Polyurethane can be adapted to comprise a wide range of unique properties, which is a key factor of its versatility. Polyurethane is extremely versatile, flexible, durable, biocompatible and biostable. Also polyurethane has a good abrasion resistance, excellent mechanical strength, good oil, grease and solvent resistant, good corrosion resistance and good heat resistance properties. Polyurethane is mainly used in many industries for a variety of applications. Polyurethane is used in a wide range of products, ranging from mattresses to plastic parts such as rigid foam insulation panels, electronics to medical application such as breathable wound dressing, surgical gowns, drapes, hospital mattresses, surgical drapes, organ retrieval bags, various medical device applications. They have been used in biomedical field for various applications due to the propensity to modify their unique properties and they are easily available materials [1]. Also, polyurethane as a used coating material.

Polyurethanes are produced by the exothermic reactions between alcohols with two or more hydroxyl (-OH) groups per molecule (diols, triols, polyols) and isocyanates. Although isocyanates play a vital role in the polyurethane synthesis (due to the differences in their reactivity depending on the presence of aromatic and aliphatic moieties) but the final property of the polyurethane is mostly determined by the type of polyol used [2]. The properties of various types of urethane polymers are dependent upon molecular weight, degree of cross-linking, effective intermolecular forces, stiffness of chain segments and crystallinity [3].

In recent years, polymer-nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components [4]. Nanoparticles have larger surface area and hence higher efficiency than larger size particles. Owing to its nanometer size and huge surface of filler nanoparticle, the interface between two phases increase dramatically and thus the interfacial interaction between filler and polymer is enhanced, which, in turn, results in a great improvement of the material properties [5]. Polymer nanocomposites have continually attracted increasing interest over the last decade, due to significant improvements they can offer compared to neat polymer matrices such as the enhancement of elastic modulus and tensile strength, as well as thermal, electrical and barrier properties of the systems [6]. Also nanoparticles increase toughness, surface hardness and improve flame resistance and antibacterial&antifungal activity properties. For a solid nanocrystal to be labelled a metal organic framework, it should play the inherent attributes that this term implies: strong bonding providing robustness, linking units that are available for modification by organic synthesis, and geometrically well-defined structure [7]. Owing to the high surface area MOF-199 can be used for sensing applications to efficiently sense various gases and biomolecules [8]. Metal organic frameworks (MOFs) are typically synthesized by combining organic ligands and metal salts in solvo-thermal reactions at relatively low temperatures (below 300◦C) [9]. As a new type of porous crystalline materials, MOFs have received huge attention in the past decade due to their unique properties, i.e. huge surface area, high porosity, low density, controllable structure and tunable pore size. A wide range of applications has included gas separation, storage, catalysis, and drug delivery benefit from the recent fast developments of MOFs [10].

Coated fabric is "a textile fabric on which there has been formed in situ, on one or both surfaces, a layer or layers of adherent coating material". Coated fabric is material composed of two or more layers, at least one of which is a textile *fabric* and at least one of which is a substantially continuous polymeric layer [11]. In many extreme climatic situations, breathable fabrics protect the human body from external heat, wind, water, and many harmful agents, and at the same time it also permits effective transmission of moist vapor from inside to outside atmosphere. Breathable fabrics passively allow water vapor to diffuse through them yet still prevent the penetration of liquid water [12]. Polyurethane is mostly used for coating the textile material. Polyurethane has good washproofness and cleaning resistance, good adhesion to the fabric, good durability at low temperatures, it is possible to use it without softeners, it has good viscosity and abrasion resistance, at the same time it has a pleasant and soft touch, a low specific mass, resistance to oils and fats [13]. Several characteristics (including flexibility and soft hand) would make polyurethane especially suited for the use in breathable textiles [14]. The main uses of this type of coating technique are the transfer coated polyurethane fabrics are in up-market and the waterproof protective clothing. Other outlets for transfer coated polyurethane include upholstery, luggage, footwear, gloves and waterproof mattress covers [15].

In this study, we have investigated the water vapor permeability and mechanical properties of PU/MOF-199 nanocomposite coated polyester fabrics. To prepare the coated fabrics, we use transfer coating method to obtain polyurethane coated fabric. In principle, transfer coating consists of applying a polymeric coating on the surface of a support, usually paper, laminating the textile substrate to be coated to the polymeric layer and removing the release paper, to yield a transferred polymeric layer on the textile [16]. Our aim is to improve the breathability of polyurethane fabric by using metal organic framework as nanofiller.

2. Materials and Method

2.1. Material

Dichloromethane (DCM, CH_2Cl_2 LAB-SCAN), triethylamine (TEA, $N(CH_2CH_3)_3$, Acros Organics), dimethylformamide (DMF, $(CH_3)_2NCOH$, LAB-SCAN), ethanol (CH_2OH, J.T. Baker), trimesic acid (1,3,5-benzenetricarboxylic acid, BTC, $C_9H_6O_6$, Acros Organics), Copper(II) acetate monohydrate ($Cu(CH_3COO)_2.H_2O$, Acros Organics), Larithane CS38S (One-component aromatic adhesive/polyether type, Novotex), Laripur 07588 (Aromatic polyurethane&polycarbonate copolymer in chips form, Novotex).

2.2. Synthesis of MOF-199

A crystalline porous copper-based metal organic framework MOF-199 was synthesized from the reaction of 1,3,5-benzenetricarboxylic acid and copper acetate monohydrate by a solvo-thermal method. Benzenetricarboxylic acid (4,7 mmol) was mixed in 24 mL of a 1:1:1 mixture of

DMF/EtOH/H_2O. $Cu(CH_3COO)_2.H_2O$ (8,07 mmol) was mixed with 24 mL of the same solvent. The two solutions were combined with stirring. Triethylamine (6,9 mmol) was added to the reaction mixture, which was stirred for 23 h at room temperature. The product was collected by filtration, washed with two times DMF and three times DCM. The product then dried at 170 °C for 6 hours, yielding MOF-199. The digital photograph and SEM micrograph of the MOF-199 are shown in Figure 1.

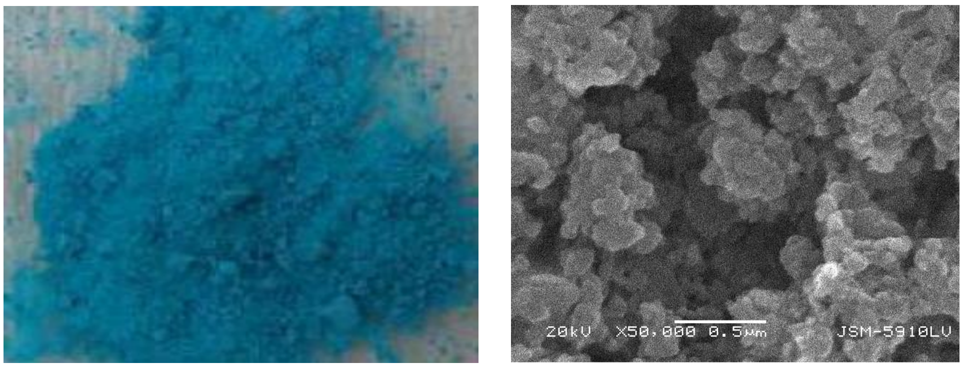

Figure 1. The digital photograph and SEM micrograph of MOF-199

2.3. Preparation of PU/MOF-199 Nanocomposites

PU/MOF-199 nanocomposites were prepared by mixing polyurethane with MOF-199 in a solvent medium. The mixtures of PU/MOF-199 nanocomposites with different MOF-199 contents were prepared in dimethyl formamid as a solvent. MOF-199 nanoparticles were dispersed into DMF. Then, the mixture of MOF-199 and DMF was stirred with magnetic stirrer for 24 hours. MOF-199 percentage was varied for 0, 1, 2, 5 10 wt. % in the total formula. The photo of PU/MOF-199 nanocomposite containing 5 wt. % of MOF-199 is shown in Figure 2.

Figure 2. The photograph of PU/MOF-199 nanocomposite solution containing 5 wt.% of MOF-199

2.4. Preparation of Coated Fabric with PU/MOF-199 Nanocomposites

Polyurethane was applied to the knitted fabric using the transfer procedure. Different amounts of MOF-199 nanoparticles (1, 2, 5, 10 wt. %) were mixed with the final polyurethane mixture. The polyurethane was spread on to silicone release paper to form polyurethane film. The coatings were adjusted in the distance between the knife on which the polyurethane paste was applied and the roller under the knife. The liquid coating was the passed through an oven to solidify the coating. The drying temperature 130 °C and the drying time is 1 minute. The weight of first layer was 30 gr/m^2. The other coating of the same polyurethane paste was applied in the same way. The final coating was an adhesive polyurethane on which the knitted fabric was laminated. The top layer was joined to the knitted fabric. The coated fabric was passed through a dryer to solidify the coating. The weight of first layer was 30 gr/m^2. The solvent was evaporated and crosslink the two layers together. This last coating acts as an adhesive. The weight of first layer was 35 gr/m^2. The coated fabrics were dried at 130 °C for 1.5 min in order to remove DMF. The coated fabric was stripped from the release paper, which can be reused. We displayed with a digital photograph of the polyurethane coating method on to fabric in Figure 2. The thickness of the coated fabric was about 0.4 mm.

Figure 3. The preparation of coated fabric with PU/MOF-199 nanocomposite

3. Results

3.1. FTIR Analyses of MOF-199

The bands around 764 cm^{-1} is attributed to Cu substitution on benzene groups and the two weak bands at 1042 and 1110 cm^{-1} are attributed to C-O-Cu stretching [17]. The zone between 1300 and 1700 cm^{-1} is related to the carboxylate ligands and is thus indicative of the coordination of BTC to the copper sites. The bands at 1645 and 1590 cm^{-1} and at 1450 and 1370 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups in BTC [18]. FTIR spectrum of MOF-199 is shown Figure 4.

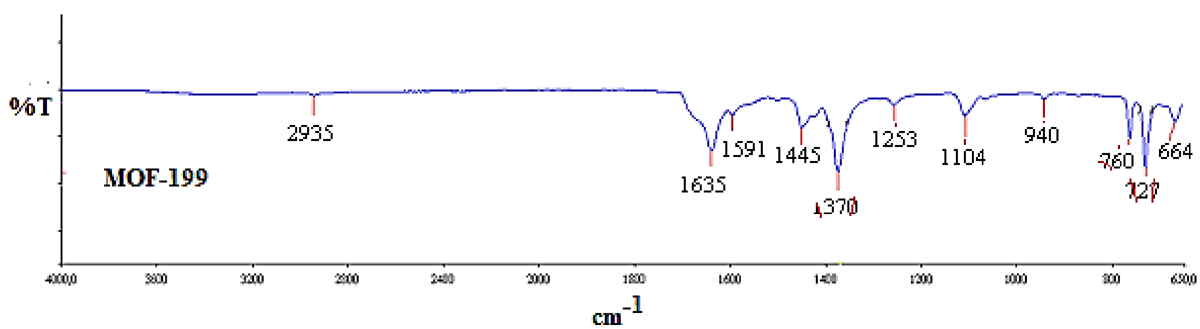

Figure 4. FTIR spectrum of MOF-199

3.2. Tensile Strength and Elongation Test Results

Tensile testing and elongation at break of the PU/MOF-199 coated fabirc was carried out using Devotrans universal testing machine with a load cell and following “ISO 1421:1998 Rubber-or plastics-coated fabrics-Determination of tensile strength and elongation at break” test method. The specimens were tested for each sample and average value taken. Tensile strength and elongation at break test results are shown in Tablo 1.

Table 1. Tensile strength and elongation at break test results

MOF Content, wt%	**Tensile Strength , N**		**Elongation at Break, %**	
	Weft	**Warp**	**Weft**	**Warp**
0	248,0	473,00	113,30	71,30
1	358,50	501,50	89,70	79,88
2	400,00	480,00	86,10	74,24
5	365,00	485,00	85,30	73,30
10	378,00	483,00	83,20	72,50

Testing tensile properties of neat PU coated fabric and PU/MOF-199 nanocomposite coated fabrics indicated that adding MOF-199 to the coating mixture result in increasing breaking force significantly for weft direction and slightly for warp direction. The influence of PU/MOF-199 coating on coated fabric properties reflects in the increasing breaking force of coated fabrics in respect to neat PU coated fabric % 44,56 on the weft direction and % 6 on the warp direction for 1 wt.% MOF-199 coating fabric. When applying PU/MOF-199 fabric coating, elongation at break slightly changes.

3.3. Tear Strength Test Results

The tear strength test was determined by using Devotrans universal testing machine at room and following “ISO 4674-1:2003 Rubber - or plastics-coated fabrics - Determination of tear resistance - Part 1: Constant rate of tear methods” test method. Tear strength test results are shown in Table 2.

Table 2. Tear strength test results

MOF Content, %	**Tear Strength, N**	
	Weft	**Warp**
0	28,67	24,67
1	34,00	30,20
2	42,50	26,6
5	38,00	25,20
10	35,00	22,50

3.4. Water Vapour Permeability Test Results

The water vapor permeability test results was measured according to ASTM E96 procedure D with the following condition 32,2°C and % 50 relative humidity. The water vapor permeability test results shown in Table 3.

Table 3. The results of water vapour permeability analyses

MOF Content, %	**WVP, g/m2. h**
0	273
1	385
2	250
5	270
10	242

Water vapor permeability of PU-coated fabrics decreased slightly with increased concentration of MOF-199, whereas only a slight increase was observed with 1 wt.% MOF-199 content.

3.5. Accelerated Ageing Test Results

Accelerated ageing testing is a test performed on materials aimed to speed up failures by the same processes the material would experience when in use. We performed accelerated testing to see how long our fabrics are likely to last when they get to work. The accelerated ageing test result was measured according to ISO BS 3424 12:1996 ISO 1419:1995 test method. According to the test method place the sample in the oven, maintained at 70 °C ± 1°C and humidity. After 168 h (7 days) at this temperature, we removed the test specimens from the oven and we examined the test pieces and record any cracks in the coating. We could not see any damage on our specimen for 8 weeks. According to accelerated ageing test, the life cycle of the PU/MOF-199 coated fabric increased slightly.

Conclusions

In this study, PU/MOF-199 nanocomposite was successfully synthesized and it was used for producing coated polyester fabric. The PU/MOF-199 nanocomposite coated fabric with varying MOF-199 percentages (1, 2, 5 and 10 wt. %) were initially tested for water vapor permeability and it was observed that about 2 wt.% MOF-199 could reduce the air permeability. The PU/MOF-199 coated fabrics show higher tear strength as compared to neat PU coated ones. The PU/MOF-199 nanocomposite coating of around 1 wt.% shows a maximum value of tensile strength, which is % 44 and 56 for weft direction and % 6 for the warp direction higher than neat PU coated fabric. Also MOF-199 was improved the coated fabric's life time compare to neat PU coated fabric.

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