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Research Article

Utilization of Waste Clay from Boron Production in Bituminous Geosynthetic Barrier (GBR-B) Production as Landfill Liner

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Bituminous geomembranes, one type of geosynthetics, include a hot bituminous mixture with mineral filler and reinforcement. In this study, boron production waste clay (CW) was used as filler to produce a geosynthetic barrier with bentonite, waste tire, and bitumen. Bentonite and waste tires were used as auxiliary fillers and bitumen as the binder. CW/bitumen, CW/bentonite/bitumen, and CW/waste tire/bitumen mixtures were prepared by using a laboratory mixer at 100°C. Hot mixtures were extruded into strips by using a lab-scale corotating twin screw extruder (*L*/*D*: 40) followed by die casting (2 mm × 100 mm). Glass fleece or nonwoven polyester was used as reinforcement material and while die casting, both sides of the reinforcement materials were covered with bituminous mixture. Thickness, mass per unit area, tensile strength, elongation at yield, and hydraulic conductivity were used to characterize the geomembranes. Among all geomembranes, nonwoven polyester covered with 30% bitumen-70% boron waste clay mixture (PK-BTM30CW70) was found to be the most promising in terms of structure and mechanical behaviour. After that, consequences of its exposure to distilled water (DW), municipal solid waste landfill leachate (L-MSW), and hazardous waste landfill leachate (L-HW) were examined to use for an innovative impermeable liner on solid waste landfills.

1. Introduction

Geosynthetic barriers, also known as geomembranes, are defined as a nonporous homogeneous material, a relatively impermeable membrane, or barrier used in a geotechnical engineering application so as to control fluid migration from a man-made project, structure, or system. In the use of geomembranes as barriers to the transmission of fluids, it is important to recognize that it differs from other liner materials that are porous such as soils and concrete. The transmission of permeating species through geomembranes without holes occurs by absorption of the species in the geomembrane and diffusion through the geomembrane on a molecular basis [1]. Bituminous geomembranes (GBR-B) are mainly composed of a binder (the modified bitumen), a filler (mostly calcite mine is used industrially), and a reinforcement (glass fleece or nonwoven polyester is preferred) as shown in Figure 1.

GBR-Bs are highly resistant to oxidation and UV rays without an antioxidant or stabilizer when compared to polymeric geomembranes (GBR-P). GBR-Ps are widely used in landfills as impermeable liner. Also the viscoelastic behavior of GBR-B allows self-repair of any defect that may occur with time such as strain, puncture, or fracture. Fillers are used in GBR-B with the intent of increasing stiffness and strength and also filling the voids in the hot mixture [2]. The filler is not only natural aggregates such as calcite, but also lime, lignin, sulfur, or ultrathin cut fiber particles which could pass number 200 (0.075 mm) sieve [3].

Turkey has 72% of the world's boron reserves and takes the first place with a reserve of 1.8 million tons. Eskisehir Eti Maden Kırka Boron Works has the largest boron reserve in

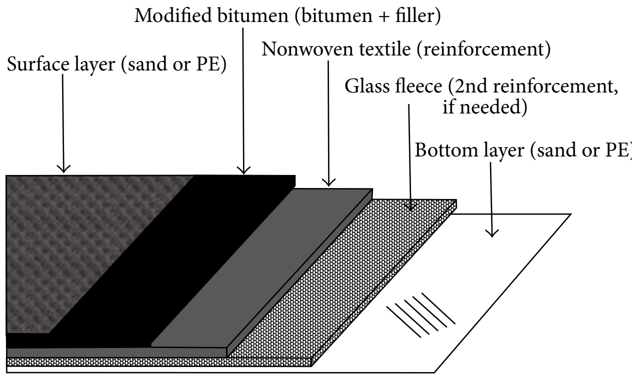


Figure 1: Bituminous geomembrane [1].

Turkey with 41% of the world's boron production. On the other hand, boron minerals have a strategic importance due to their wide range of uses in the manufacture of industrial products including glass, ceramic, textile, detergent, metallurgical, and fire-retardant materials. Thus, 900.000 tons of boron derivative waste are generated during 1 million-ton borax pentahydrate production [4]. Increasing amount of mining wastes, storage, stability, and safety of waste, and air, soil, and water pollution are major environmental issues [5]. Under the circumstances, developing novel products from the waste clay and investigating the utilization areas for waste clay become a necessity.

There have been studies related to utilization of the clay derivative waste and concentrated waste from boron concentrator facilities in various sectors such as cement [6–11], construction, brick and tile [12–20], and ceramic [21, 22]. Among these various studies, to our best knowledge, utilization of boron waste clay as a filler material has not been studied. Therefore, in this study, boron production waste clay (CW) was used as filler to produce a geosynthetic barrier with bentonite, waste tire (TW), and bitumen. Bentonite and waste tires were used as auxiliary fillers and bitumen was used as the binder.

2. Materials and Methods

2.1. Materials. Waste clay samples used in this study were collected from Eti Maden Kırka Boron Works in Eskisehir, Turkey. Basic geotechnical properties of the waste clay were given in Table 1. Grain-size distribution of CW consists of 1.74% sand, 20.76% silt, and 77.5% clay and the determined soil class is high plasticity clay (CH). CEC of the CW is 55 meq/100 g and this kind of high CEC values denotes that the clay is able to hold more contaminants. According to XRD, XRF, ICP-MS, and FT-IR results, dolomite is the most dominant compound in the CW followed by magnesium oxide, tincal, and quartz. The specific surface area of the CW is $5.12 \pm 0.1\ m^2/g$ by BET analysis method. The analyses methods and the details of the properties are available in our previous study [23].

Bitumen is used on the purpose to coalesce and unite the clay particles. The properties of bitumen (penetration 100/150 at 25°C, 100 g, 5 sec; softening point 39–47°C; flash point 230°C), the binder of the hot mixtures, were adopted from Turkish Petroleum Refineries Corporation (TÜPRAŞ), Turkey. Bentonite is generally used in improvement of impermeable compacted clay layers in landfills due to its high swelling potential and low hydraulic conductivity [24]. Bentonite was obtained from a bentonite plant. In this study, it is aimed at utilizing waste tires in landfill sites as a side material using boron waste clay. The particle size of the adopted waste tire samples was less than 1.18 mm. The steel free waste tire (<1.18 mm) was adopted from a tire recycling plant. Two different reinforcement materials were used, fiberglass tissue also known as glass fleece (CT) and nonwoven polyester (PK), and both were obtained from a geomembrane production plant.

2.2. Geomembrane Production. In the geomembrane production process, bitumen was firstly mixed with auxiliary fillers, bentonite or waste tire within a laboratory mixer at 100°C. After obtaining a homogenous mixture waste clay was added at certain amounts given in Table 2 and mixed for 45 minutes. In addition to geomembrane samples including bentonite or waste tire, neat samples including only CW were also prepared.

After mixing, hot mixtures were extruded into strips by using a lab-scale corotating twin screw extruder (*L/D*: 40) followed by die casting (2 mm × 100 mm). The temperatures of the various barrel elements were set in the ranges 100–130°C (bitumen introduction) and 38–52°C (extruder exit). Depending on the ingredients amount, the apparent fluidity of hot mixtures differed from each other. In order to obtain optimum product with stabile strip shape and no visible deformations such as puncture, tearing, or ruffle, different heating profiles were constituted for each mixture.

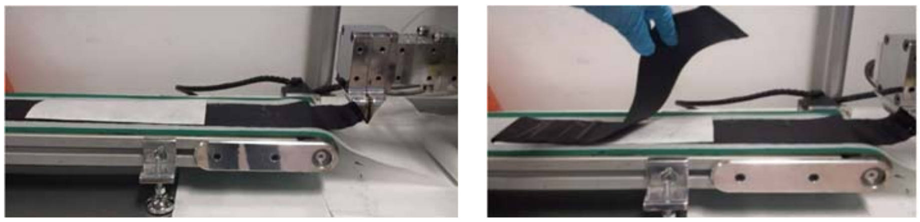
The extruded strips were then passed on a conveyor belt at a speed of 1 rpm. Two different reinforcement materials were used, fiberglass tissue also known as glass fleece (CT) and nonwoven polyester (PK). When the optimum profile was obtained, reinforcement material was placed on the binder mixture in strip shape and another layer of strip was placed on the reinforcement and pressed. Thus, both sides of the reinforcement material were covered with bituminous mixture (Figure 2).

2.3. Analyses Performed on GBR-B. According to the Turkish Standard of "TS EN 13493: Geosynthetic barriers-Characteristics required for use in the construction of solid waste storage and disposal sites," thickness (TS EN 1849-1), mass per unit area (TS EN 1849-1), tensile strength (TS EN 12311-1), elongation at yield (TS EN 12311-1), and hydraulic conductivity (TS EN 14150) tests were applied to geomembranes with/without reinforcements to see the effect of reinforcements.

The tensile properties are the most critical mechanical properties of geomembranes since there are a range of tensile forces that can act on the geomembrane during installation and service. Also it is misleading to assume that if a geomembrane material has a high elongation at break, it

Table 1: Geotechnical properties of CW.

Water content, %	Specific weight, g/cm^3	Liquid limit, %	Plastic limit, %	Plasticity index, %	Optimum water content, %	Unconfined compressive strength, kg/cm^2	Hydraulic conductivity, m/s	Swelling potential, %
39.2	2.77	58	30	28	33	2.16	3.5×10^{-11}	10.4



(a) (b)

Figure 2: Geomembrane production with lab-scale extruder.

Table 2: BTM/CW, BTM/CW/BNT, and BTM/CW/TW specimens and proportions.

Specimen code	BTM, %	CW, %	BNT, %	TW, %
BTM30CW70	30	70	—	—
BTM40CW60	40	60	—	—
BTM50CW50	50	50	—	—
BTM40CW50BNT10	40	50	10	—
BTM40CW52BNT8	40	52	8	—
BTM40CW55BNT5	40	55	5	—
BTM40CW50TW10	40	50	—	10
BTM40CW52TW8	40	52	—	8
BTM40CW55TW5	40	55	—	5

BTM: bitumen; CW: waste clay; BNT: bentonite; TW: waste tire
All numbers in specimen codes represent the percentage of material at its left in the mixture.

has high survivability in service. Elongation at yield of the geomembrane should be investigated instead of elongation at break because after yield elongation point, deformation is irreversible. For instance, high density polyethylene (HDPE) has an elongation at break value of 700% but exhibits a distinct yield point at 12% strain [1]. According to the tensile and elongation properties, one of the BTM/CW, BTM/CW/BNT, and BTM/CW/TW geomembranes was selected to apply hydraulic conductivity test (Figure 3).

2.4. Exposure to Leachate. Leachate tests were applied to the most promising geomembrane sample determined by the analyses according to TS EN 13493. Geomembrane sample was exposed to distilled water (DW), municipal solid waste landfill leachate (L-MSW), and hazardous waste landfill leachate (L-HW). L-MSW was collected from a municipal solid waste landfill and L-HW was collected from İzmit Waste and Residue Treatment Incineration Recycling Co. (İZAYDAŞ). The test arrangement constituted for geomembranes exposure to leachate (Figure 4(a)) included a hydraulic conductivity test cell (Figure 4(b)) which was composed of two parts (*D*: 50 mm) holding to each other by clamping for housing the geomembrane sample. In Figure 4(a), 1 bar of pressure was constantly applied on the leachate column to sustain the 1-bar fluid pressure in test cell. The plastic bottle on the bottom is placed for collecting leachate sample from the exit stream of the cell in case of any leaching occurrence. The leachate exposure test lasted for 35 days. SEM analysis was performed to examine the structural changes on the surface of geomembrane specimen due to exposure to leachates by using Phenom ProX SEM. Before the analysis, in order to prevent electrical charging, geomembrane was covered with gold for 40 seconds under the presence of Argon gas. During the analysis, 300, 500, and 1000x zoomed SEM images were obtained for each geomembrane and the appropriate 2 images in all 3 were chosen for consideration.

3. Results and Discussion

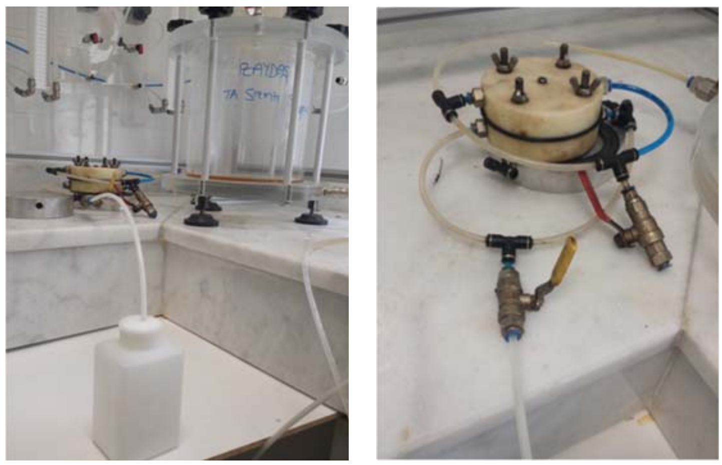
Results of thickness, mass per unit area, tensile strength, and elongation at yield analyses performed on geomembrane samples with/without reinforcement are given in Table 3. A commercial geomembrane was also tested in order to compare the results of produced geomembranes.

According to Table 3, geomembrane samples had thickness values between 2.5 and 3.7 mm. These thickness values are in the range of 2 to 5 mm given by the literature [1]. Produced samples had mass per unit area values between 3.6 and 5.4 kg/m^2. Geomembranes with mass per unit area above 0.5 kg/m^2 are considered as heavyweight membranes since this specification depends on density of the reinforcement and the filler [1].

Tensile strength of the geomembrane samples without reinforcements decreases with increasing bitumen content; in other words, tensile strength increases with increasing waste clay content.

Bentonite addition improved neither tensile strength nor elongation of geomembrane. At constant bitumen content, decreasing bentonite content and increasing waste clay

Figure 3: Hydraulic conductivity test arrangement.



(a) (b)

Figure 4: Leachate test arrangement: (a) leachate column; (b) test cell.

content affected tensile strength values of geomembrane negatively.

Waste tire addition improved tensile strength when bitumen/waste clay/waste tire mixtures were examined. At constant bitumen amount, tensile strength of the geomembrane increased with increasing waste tire amount. So with the intent of utilizing waste tires, waste tire could be used in geomembrane materials as modifier of bitumen.

Glass fleece reinforced geomembranes, in other words the CT-specimens, had relatively higher tensile strength values. However elongation values were in the range of 5–8% which was very low when compared to the commercial geomembrane.

The highest elongation belonged to PK-BTM30CW70 and PK-BTM50CW50, where nonwoven polyester reinforcement is already known to have a beneficial usage in geomembranes due to its high yield elongation. Tensile strength of PK-specimens was also higher than the commercial bituminous geomembrane. Therefore, PK (nonwoven polyester) was considered as the most appropriate reinforcement material. Since all specimens with PK had favorable tensile strength and elongation values, the one with highest waste clay content among BTM/CW, BTM/CW/BNT, and BTM/CW/TW groups was selected for hydraulic conductivity test application.

Hydraulic conductivity test was performed with PK-BTM30CW70, PK-BTM40CW55BNT5, and PK-BTM40CW55TW5. The hydraulic conductivity test results were 3.6×10^{-6}, 2.2×10^{-5}, and $1.0 \times 10^{-5}\,m^3/m^2$/day, respectively, while the hydraulic conductivity of commercial geomembrane was $10^{-6}\,m^3/m^2$/day. PK-BTM30CW70 had the closest value to commercial geomembranes' value; hence leachate exposure tests were performed with only that specimen.

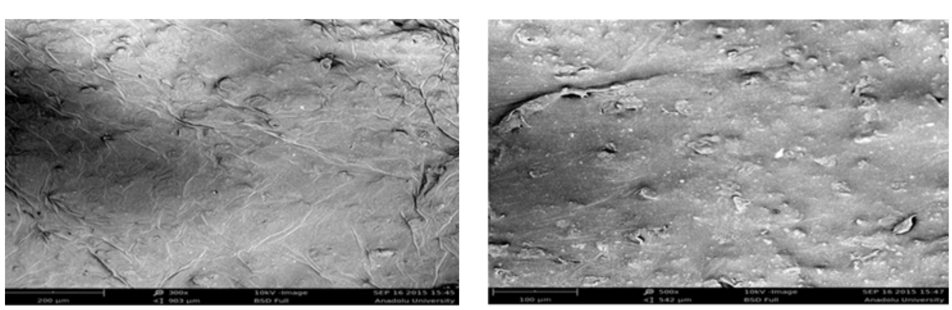
3.1. Exposure to Leachate Results. Leachate exposure tests were carried on with PK-BTM30CW70 for 35 days. Meanwhile, leaching of any water sample through geomembrane was not observed; the outlet tubes and sample bottles were both empty at the end of the experiment. This result was a proof of considerably low hydraulic conductivity of the produced geomembrane. SEM analysis was performed on uncured geomembrane (Figure 5) and geomembrane samples exposed to DW (Figure 6), L-MSW (Figure 7), and L-HW (Figure 8).

SEM images of uncured geomembrane show a solid structure without any scratch, puncture, or gaps. Here, waste clay seems to be distributed homogenously in the mixture and size of waste clay particles is in the range of 10–20 μm.

Table 3: Physical properties of all specimens and constituents.

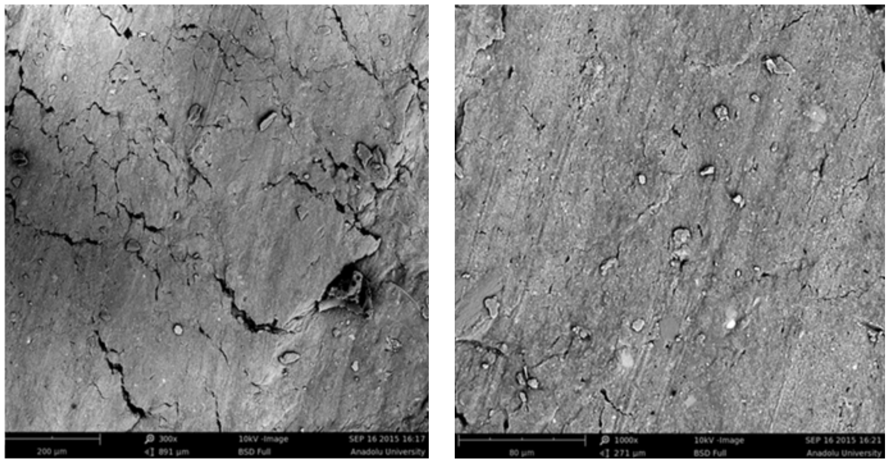
Reinforcement state	Specimen	Thickness (mm)	Mass per unit area (kg/m^2)	Tensile force (kN)	Elongation (%)
Without reinforcement	BTM30CW70	1.4	2.2	0.0033	20
	BTM40CW60	1.3	2.0	0.0022	20
	BTM50CW50	1.2	1.8	0.0010	20
	BTM40CW50BNT10	1.4	2.3	0.0010	20
	BTM40CW52BNT8	1.4	2.5	0.0012	20
	BTM40CW55BNT5	1.5	2.7	0.0013	20
	BTM40CW50TW10	1.5	2.3	0.0029	50
	BTM40CW52TW8	1.5	2.5	0.0022	30
	BTM40CW55TW5	1.7	2.6	0.0022	32
With reinforcement					
Glass fleece	Glass fleece	0.25	0.044	0.1045	1.4
	CT-BTM30CW70	3.2	4.4	0.5152	7
	CT-BTM40CW60	2.7	4.0	0.6386	7
	CT-BTM50CW50	2.8	3.6	0.4606	7
	CT-BTM40CW50BNT10	3.0	5.4	0.5520	7
	CT-BTM40CW52BNT8	3.1	4.9	0.5735	8
	CT-BTM40CW55BNT5	3.2	4.6	0.6000	7
	CT-BTM40CW50TW10	3.2	4.6	0.3104	5
	CT-BTM40CW52TW8	3.7	5.0	0.5606	7
	CT-BTM40CW55TW5	3.6	5.2	0.4860	7
Nonwoven polyester	Nonwoven polyester	0.5	0.148	0.3885	40
	PK-BTM30CW70	3.2	4.5	0.4928	68
	PK-BTM40CW60	2.5	4.1	0.4213	57
	PK-BTM50CW50	3.0	3.7	0.4830	68
	PK-BTM40CW50BNT10	3.1	4.7	0.4061	53
	PK-BTM40CW52BNT8	3.4	5.0	0.4624	62
	PK-BTM40CW55BNT5	3.4	5.5	0.4964	67
	PK-BTM40CW50TW10	3.2	4.7	0.5088	35
	PK-BTM40CW52TW8	3.5	5.1	0.4935	59
	PK-BTM40CW55TW5	3.6	5.3	0.4986	59
Commercial geomembrane		3.2	3.6	0.4032	75

BTM: bitumen; CW: waste clay; BNT: bentonite; TW: waste tire; PK: nonwoven polyester; CT: glass fleece
All numbers in specimen codes represent the percentage of material at its left in the mixture.



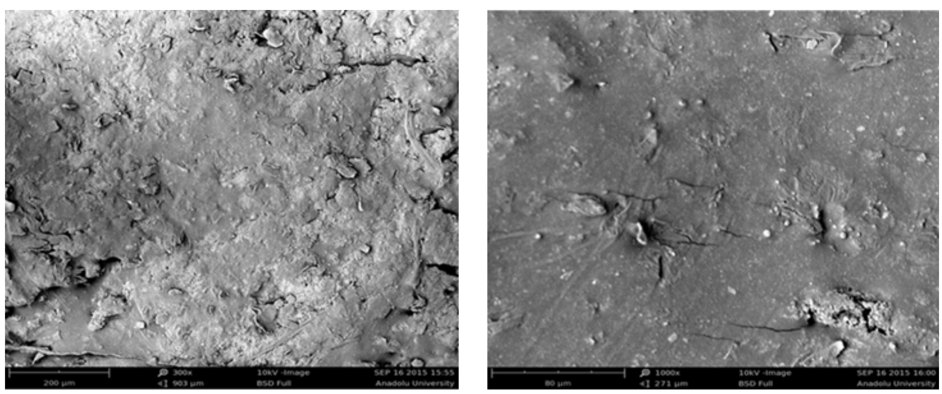
(a) (b)

Figure 5: SEM images of uncured PK-BTM30CW70: (a) 300x; (b) 500x.



(a) (b)

Figure 6: SEM images of PK-BTM30CW70 exposed to DW: (a) 300x; (b) 1000x.



(a) (b)

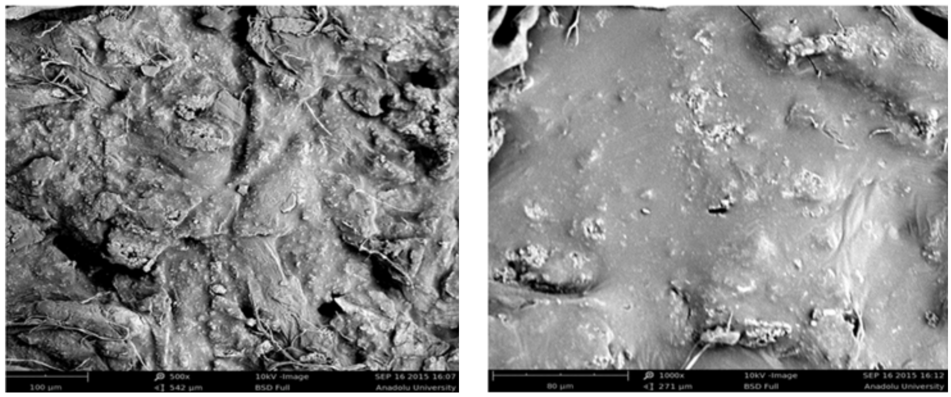
Figure 7: SEM images of PK-BTM30CW70 exposed to L-MSW: (a) 300x; (b) 1000x.

Geomembrane sample exposed to distilled water had some scratches with maximum length of 200 μm and a small amount of waste clay was released from the bitumen and reached the surface. Geomembrane exposed to L-MSW had 200 μm scratches and also fractional punctures with the length range 10–20 μm. Geomembrane exposed to L-HW had a relatively more defective image with punctures at length of 20–50 μm. Clay particles that reached surface were observed more in those images. The punctures are claimed to be a result of a certain amount of waste clay released from the bitumen when the geomembrane gets in contact with any kind of water. However those defects were limitative on the top surface of the geomembrane. Additionally, any effect on the bottom was not expected since no leaching was observed.

4. Conclusion

In this study, waste clay generated during boron derivatives production was mixed with bitumen, bentonite, and waste tire and these mixtures were used to cover up reinforcement materials (nonwoven polyester and glass fleece). Among all produced geomembrane samples, according to thickness, mass per unit area, tensile strength, and elongation results, the samples were eliminated by comparing to a commercial geomembrane and only three samples (PK-BTM30CW70 (nonwoven polyester, 30% bitumen, 70% waste clay), PK-BTM40CW55TW5 (nonwoven polyester, 40% bitumen, 55% waste clay, and 5% waste tire), and PK-BTM40CW55B5 (nonwoven polyester, 40% bitumen, 55% waste clay, and 5% bentonite)) were used to apply hydraulic conductivity test. PK-BTM30CW70 was determined as the optimum geomembrane with the lowest hydraulic conductivity. Therefore leachate exposure tests were performed with PK-BTM30CW70 and distilled water, municipal solid waste leachate, and hazardous waste leachate. During the experiments, leaching did not occur, but SEM analysis comparison of geomembranes exposed to leachate showed increasing defectives such as scratches and punctures. Those structural defects did not affect the impermeability of geomembrane.

In terms of tensile strength, elongation, and hydraulic conductivity, boron waste clay could be used in geomembrane production instead of calcite in order to lower the cost



(a) (b)

Figure 8: SEM images of PK-BTM30CW70 exposed to L-HW: (a) 500x; (b) 1000x.

while leading up to utilize waste clay of 900,000 tons/year generated at boron enterprises in Turkey. The optimum geomembrane produced is appropriate to use in landfills in means of the applied test results. As a conclusion, this study has an importance from the point of sustainable waste management principles with its aim to produce an innovative material by using waste materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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