Investigation of dehydrogenation performance and air stability of MgH_2 –PMMA nanostructured composite prepared by direct high-energy ball-milling

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Abstract

Mechanical milling and a gas-selective polymer were used to protect MgH_2 from oxidation and improve its dehydrogenation properties. MgH_2 and poly(methyl methacrylate) (PMMA) were simultaneously ball-milled for 5 and 20 h, respectively, to prepare an air-resistant nanostructured composite. The properties of the nanostructured composite were studied by XRD, SEM, and FTIR methods. The dehydrogenation performance of all samples was investigated by TGA analysis. The hydrogen desorption performance of ball-milled samples was also evaluated after exposure to air for 4 weeks. Results showed that MgH_2 desorbed about 0.79 wt.% of hydrogen after heating up to 300 °C and holding for 15 min at this temperature. The ball-milling of MgH_2 and PMMA for 5 and 20 h led to hydrogen desorption of 6.21 and 6.10 wt.% after heating up to 300 °C and holding for 15 min at this temperature, respectively, which proved the surface protection of MgH_2 from oxidation by PMMA. After 4 weeks of exposing the ball-milled MgH_2 –PMMA samples to air, their hydrogen desorption percentage at the same condition changed to 5.80 and 5.72 wt.% for 5 and 20 h milled samples, respectively. A slight reduction in the dehydrogenation percentage of air-exposed samples proved that the air stability of MgH_2 had been significantly enhanced by its confinement with PMMA.

Keywords Hydrogen storage · MgH_2 · PMMA · Nickel catalyst

Introduction

Nowadays, the growing use of fuels such as oil, natural gas, and coal in different industries has become a global problem due to ecological concerns and depletion of resources. Some scientific efforts have introduced H_2 as a clean and renewable energy platform for the substitution of fossil fuels. Recently, hydrogen has attracted worldwide attention as a new energy carrier. It has already found applications in experimental cars as fuel, and major automobile companies

are planning to build a car that uses hydrogen fuel. Hydrogen is currently used as the fuel of choice for space programs around the world [1]. Finding a proper method for H_2 storage and release is a key challenge in this technology [2].

Liquid and metal hydride has been considered for solving the problem of hydrogen storage, but none of these methods are used widely as a commercial solution [3]. Gas- and liquid-state storage is encountered with problems such as safety issues, low volumetric energy density, and high cost of containers, while solid-state storage has some advantages in this regard [4]. Hydrogen storage in the format of strong chemical hydride bonds in solids is a solid-state storage method, and metal hydrides such as MgH_2 and LaNi_5H_6 [5–7] and complex hydrides such as LiBH_4 , NaBH_4 and NaAlH_4 [8–10] are some of the most promising hydride materials for solid-state hydrogen storage. Light and clean metal hydride batteries are already commercially available for laptop computers, and larger-capacity batteries are being developed for electrical cars [1]. Among the hydride solids, MgH_2 is a compelling candidate for solid-state hydrogen storage because of

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earth abundance, relative cost-effectiveness, non-toxicity, acceptable theoretical hydrogen storage capacity, and reversibility [11, 12]. Some hydrides such as LiAlH_4 and BH_3 perform the hydrogen storage process with better storage density, but characteristics such as adsorption–desorption reversibility, regeneration ability, and lower formation enthalpy are the advantages of MgH_2 compared to hydrides with a higher hydrogen storage capacity [13]. The most important limitation for the hydrogen storage performance of MgH_2 is its high decomposition enthalpy, which makes the dehydrogenation process possible only in difficult thermodynamic conditions (350 °C and 1 bar) [14]. Even if this circumstance is met, the kinetic constraints are still a problem [15]. Based on the literature, some techniques have been developed for the improvement of thermodynamics and kinetics of MgH_2 hydrogen storage performance. The most important techniques are adding catalysts and alloying materials to MgH_2 , using methods to decrease the grain or particle size of MgH_2 in the range of nanometer, and amorphization of the structure [5]. Using mechanical milling for synthesizing nanostructured MgH_2 is commonly utilized in studies [16]. This process improves MgH_2 storage characteristics by decreasing particle and grain size and increasing grain boundaries, structural defects, and surface active sites [17,18].

Huot et al. [19] investigated the effect of ball-milling on the hydrogen desorption kinetics of MgH_2 . They found that 30 h of mechanical milling led to an increment of the specific surface area of MgH_2 up to 10 times and decrement of desorption activation energy from 156 to 120 kJ/mol. They also reported a 56 °C decrease in desorption temperature of MgH_2 after 30 h of milling. A comparison between the characteristics of bulk and ball-milled MgH_2 performed by Wagemans et al. [20] showed that crystalline size reduction made by milling led to a decrement of desorption temperature from above 300 to about 200 °C.

The next commonly used method for improvement of MgH_2 hydrogen storage performance is catalyzing hydride with additives. Conventional transition metals such as Ni, Cu, V, Co, Fe, Mn, and Ti are the most practical additives used as catalyst agents for MgH_2 [4]. In the literature, catalyzing this hydride with rare earth metals [14, 23, 24] or metal oxides such as TiO_2 , V_2O_5 , Cr_2O_3 and Al_2O_3 [23, 24] has been investigated. The synergistic use of metals, oxides, intermetallic, and C-based materials is also a commonplace method for MgH_2 catalyzing [4]. Pourabdoli et al. [12] investigated the hydrogen desorption characteristics of MgH_2 catalyzed with 9Ni–2Mg–Y additive and observed a notable decrement in activation energy and onset temperature of desorption in the catalyzed sample compared with the sole ball-milled MgH_2 . Enhancement of hydrogen storage properties of MgH_2 with cobalt and CNT as the catalyst was studied by Veron et al. [25]. They reported a 55 °C

decrease in desorption temperature due to adding single Co, and 136 °C by the simultaneous presence of Co and CNT. They also showed a significant decrement in desorption time and energy due to the synergistic effect of both catalysts.

Besides the thermodynamics and kinetics limits, the high sensibility of MgH_2 to air is another constraint in its storage performance. It means that Mg and MgH_2 have very weak air stability. When Mg or MgH_2 has been exposed to an oxidant atmosphere, even with a low oxygen/humidity percentage, an impermeable and rigid layer of MgO/Mg(OH)_2 is formed on the surface of the material which prevents the diffusion of hydrogen molecules and diminishes the adsorption/desorption capacity of hydrogen [4, 26]. A practical method for the enhancement of MgH_2 air stability is using a gas separator polymer membrane that provides a selective permeability property in MgH_2 . These polymers, based on their surface pore sizes, are able to manage the diffusion of different gases according to the size of their molecules [27]. The ability of selective diffusion of H_2 from these polymers is determined with a parameter named permeability ratio (H_2/O_2 or $\text{H}_2/\text{H}_2\text{O}$) [2]. A higher permeability ratio means a lower contact between MgH_2 surface and $\text{O}_2/\text{H}_2\text{O}$ molecules and, consequently, better protection of MgH_2 surface against MgO/Mg(OH)_2 formation. The most widely used polymers for this purpose are poly-methyl methacrylate (PMMA), polyvinylpyrrolidone (PVP), and acrylonitrile-butadiene styrene (ABS), whose confinement, as an air stabilizer agent, with metal hydrides has been studied in the literature [2, 13, 27–34]. Rapee Gosalawit-Utke et al. [27] claimed that confinement of $2\text{LiBH}_4\text{-MgH}_2$ in the resorcinol–formaldehyde carbon aerogel scaffold material improved hydrogen desorption kinetics compared to bulk $2\text{LiBH}_4\text{-MgH}_2$. They stated that the nanoconfined $2\text{LiBH}_4\text{-MgH}_2$ releases 90% of the total hydrogen storage capacity within 90 min. Meanwhile, the bulk material released only 34% (at $T=425$ °C and $p(\text{H}_2)=3.4$ bar). Yuan et al. [28] reported that nanoparticles of $\text{Mg}_{95}\text{Ni}_5$ embedded by PMMA by means of milling in the PMMA solution exhibit a good air-stable property. The synthesized nanocomposites needed 60 min to absorb 3.37 wt.% hydrogen at a low temperature of 473 K. It desorbed 1.02 wt.% hydrogen within 120 min at the same temperature. The starting temperature of desorption of this composites was about 373 K. It is reported that the confinement of LiBH_4 in the PMMA and the interaction between the B atom in LiBH_4 and the O atom in C=O led to the lower hydrogen release temperature of LiBH_4 . The onset temperature of dehydrogenation of the $\text{LiBH}_4\text{-PMMA}$ composite was 53 °C. This composite released 5.2 wt.% of hydrogen at 162 °C within 1 h [29]. Makridis et al. [32] reported that laser ablation can be used for the production of single-phase, fine nanoparticles of metal hydrides. The encapsulation of the Mg-nanoparticles in a polymer matrix led to ~6 wt.% adsorption of hydrogen at a very high speed (< 20 min at

250 °C). Pentimalli et al. [33] produced LaNi_5 -type-based composite with polymers through an innovative bulk and low-cost processing approach by combining high-energy ball-milling and extrusion techniques. The composites were used as fixed beds in the implementation Cooling System. Then, the system was integrated into a refrigerated transportation vehicle. They reported good hydrogen adsorption/desorption properties in this system. Yao et al. [34] prepared polyvinylpyrrolidone (PVP)-coated $\text{Mg}_{95}\text{Ni}_5$ nano-composites by hydriding combustion synthesis plus wet mechanical milling (WM) with tetrahydrofuran (THF). They reported that the peak temperature of dehydrogenation of MgH_2 in the milled $\text{Mg}_{95}\text{Ni}_5$ decreased from 293.0 °C without THF to 250.4 °C with THF. The synthesized composites showed significant dehydriding properties.

The conventional preparation method of Mg -PMMA (MgH_2/PMMA) composite is the route adopted by Jeon et al. [2] that is repeatedly applied by other researchers. This route involves the reduction of bis(cyclopentadienyl)magnesium (Cp_2Mg) with lithium naphthalide in a solution of tetrahydrofuran (THF) containing PMMA under stirring (or wet ball-milling) in an inert atmosphere. Drying the resultant solid product leads to Mg -PMMA complete formation [2]. This chemical procedure leads to the preparation of Mg -PMMA composite with excellent microstructural characteristics and significant hydrogen storage performance, but it can be reasonable to find an alternative process, which is more cost-effective and consumes less chemical materials, to synthesize this composite.

Pentimalli et al. [35] prepared LaNi_5 -acrylonitrile butadiene styrene (ABS) composite via ball-milling of starting powders (not wet milling of THF-based suspension). It seems that this process, which is only used by these authors, can be developed and optimized as a simple and cost-effective route for many Mg -polymer composites. The synthesized composite did not show significant losses in adsorption capacity or kinetic properties. They stated that the polymeric matrix was stable under hydrogen cycling. With these explanations, the main goal of the present study was to prepare MgH_2 -PMMA via direct ball-milling of MgH_2 and PMMA

Table 2 TGA condition for all samples

Heating condition Sample	Up to 450 °C	Up to 300 °C + 15-min holding at 300 °C
PMMA	–	✓
MNB–M5–M20	✓	–
M5P–M20P–M5PA–M20PA M2N5P–M5N5P	–	✓

powders and investigate the hydrogen desorption performance of the produced nano-structured powder, especially in terms of air stability enhancement (Tables 1, 2).

Materials and research process

Starting materials used for the preparation of samples were MgH_2 (Sigma Aldrich, hydrogen storage grade, > 95% Purity, particle size < 50 μm) and PMMA (Sigma Aldrich, > 98% purity, particle size < 250 nm), and nickel (> 99% purity, agglomerates size < 10 μm , particle size < 4 μm). High-energy ball-milling was performed for mechanical activation of various mixtures including MgH_2 and MgH_2 -PMMA under argon atmosphere in a planetary ball-mill (model PM2400, Asia Sanaat Rakhsh, Iran) with 150 ml hardened steel vials, rotation speed of 250 rpm, and ball-to-powder mass ratio of 10:1. The milling process stopped for 20 min in 1 h intervals to prevent the temperature from rising. All samples and their preparation process can be observed in Table 3.

A high percentage of PMMA was chosen to complete the protection of MgH_2 against air. Furthermore, using a high percentage of PMMA may increase the number of adsorption/desorption cycles with suitable protection. It seems that if PMMA is used in small percentages, due to the weight loss of PMMA during heating, the protection of surface by PMMA disappears after a few adsorption/desorption cycles. Two samples of M5P and M20P were

Table 1 Ball-milling condition for all samples

Starting material	First milling	The added PMMA (polymer to MgH_2 mass ratio 4:1)	Second milling (polymer + MgH_2 or MgH_2 +Ni)	Sample code
MgH_2	–	–	–	MNB
MgH_2	5 h	–	–	M5
MgH_2	20 h	–	–	M20
MgH_2	5 h	✓	2 h	M5P
MgH_2	20 h	✓	2 h	M20P
MgH_2 + 2wt.% Ni	5 h	✓	2 h	M2N5P
MgH_2 + 5wt.% Ni	5 h	✓	2 h	M5N5P

Table 3 Results of crystallite size, lattice strain, and average particle size measurements of different samples

Sample	Crystallite size (nm)	Lattice strain (%)	Average particle size (nm)
MNB	154	0.07	33,200
M5	56	0.75	605
M20	34	0.90	558
M5P	41	0.82	446
M20P	33	0.94	441

also exposed to air for 4 weeks to investigate the effect of a high percentage of PMMA on the air stability of MgH_2 ; these samples were named M5PA and M20PA, respectively. Finally, 2 and 5 wt.% nickel was added to the M5P sample (M2N5P and M5N5P, respectively) to examine the effect of catalyst addition on the hydrogen desorption of the M5P sample. In these tests, at first, MgH_2 and Ni powder were milled for 5 h, and subsequently, the milled mixture was further milled with PMMA for 2 h.

The structural characterization of different powders was performed via the XRD method using a Philips PW3040/60 X-ray diffractometer (40 kV, 10 mA and $\text{Cu K}\alpha$, $\lambda = 0.1541$ nm) with the step size of 0.02° and X'Pert High Score Plus v2.2b (PANalytical Company). The mean crystallite size and the lattice microstrain of the particles were measured using the Williamson-Hall method [36]:

$$\beta_{\text{sample}} \cos \theta = K\lambda/\delta + 2\epsilon \sin \theta, \quad (1)$$

where β_{sample} is the full width at half-maximum (FWHM) of the milled powder, θ is the position of peak maximum, K is the Scherrer constant (about 0.9), λ is the beam wavelength, δ is the crystallite size, and ϵ is the lattice microstrain introduced by ball-milling. For instrumental correction, a Gaussian relationship was used [36]:

$$\beta_{\text{sample}} = \sqrt{\beta_{\text{experimental}}^2 - \beta_{\text{instrumental}}^2}, \quad (2)$$

where $\beta_{\text{experimental}}$ is the measured FWHM of the annealed powders.

The microstructural characteristics of each sample were studied by field-emission scanning electron microscopy (FESEM) using an FEI NanoSEM 450 instrument. The particle size analysis was performed by ImageJ software, based on FESEM micrographs and 20–45 measurement for different samples. Moreover, for the identification of PMMA and the study of milling effect on MgH_2 -PMMA behavior, FTIR spectroscopy was employed by a Thermo-Electron (model AVATAR, USA) instrument.

The dehydrogenation behavior of various samples was investigated by thermogravimetric analysis (TGA) using

a PerkinElmer, model STA6000 machine. The condition of thermal analysis for each sample is shown in Table 4 in detail.

All the dehydrogenation experiments with the TGA method were performed under an argon atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. To determine the mass reduction of milled PMMA in the temperature range of 0 – 300°C , the TGA diagram of single milled PMMA was recorded. Subsequently, the TGA diagrams for all MgH_2 and MgH_2 -PMMA samples were presented after the subtraction of the milled PMMA diagram for the accurate calculation of the desorbed hydrogen percentage from MgH_2 . Since MgH_2 -PMMA samples have 20 wt.% MgH_2 , the theoretical dehydrogenation capacity of MgH_2 -PMMA composites is $0.2 \times 7.6\% = 1.52\%$.

Results and discussions

Structural evaluations

The main process in this study was the ball-milling of different mixtures of MgH_2 and MgH_2 -PMMA. Thus, it seems reasonable to investigate the effect of mechanical milling on the structural and microstructural properties of each sample. The XRD patterns of as-received (MNB) and milled MgH_2 (M5, M20) and milled MgH_2 -PMMA (M5P, M20P) powders are illustrated in Fig. 1. Similar to our previous study, the MNB pattern exhibits a major phase as MgH_2 with some low-intensity peaks of Mg as the minor phase, which is common for hydrogen storage grade MgH_2 [37]. Peak broadening and decrement of their intensity are discernible in milled samples due to structural disordering, crystallite size decrement, and lattice strain increment as a result of mechanical milling [18, 22]. It is obvious that these phenomena are more notable in the M20 sample milled for a longer time compared with the M5 sample. The results of crystallite size and lattice strain calculation can be observed in Table 5. Some minor peaks of MgO can be observed in the M5 and M20 samples which indicate the partial oxidation of MgH_2 during milling or performing the XRD experiment. The XRD pattern of milled MgH_2 -PMMA samples shows peaks with more intensity decrement and width increment due to the longer milling time. Furthermore, the specific low-intensity peak of PMMA is obvious in $2\theta = 15.176^\circ$ in both M5P and M20P. It can be noted that MgO peaks in M5P and M20P samples are probably the same ones that existed in M5 and M20 samples, because 80%wt of PMMA might protect MgH_2 against further oxidation.

Figure 6 depicts the SEM images of as-received MgH_2 , PMMA, milled MgH_2 and milled MgH_2 -PMMA for different times. The MNB sample (Fig. 6a) micrograph

Table 4 Weight loss percentage and desorption onset temperature due to the dehydrogenation and weight loss percentage of PMMA in similar conditions

Sample	Decrease in wt.% Up to 450 °C	Decrease in wt.% of MgH ₂ Up to 300 °C (max decrease of MgH ₂ = 7.6%)	Decrease in wt.% MgH ₂ Up to 300 °C + 15-min holding (max decrease of MgH ₂ = 7.6%)	Desorption onset Temperature (°C)
MNB	—	—	0.79	421
M5	2.46	0	—	405
M20	3.37	0	—	370
M5P	—	3.25	6.21	180
M20P	—	3.11	6.10	175
M5PA	—	2.76	5.80	184
M20PA	—	2.59	5.72	181

shows large particles ($> 30 \mu\text{m}$) with irregular shapes. Based on Fig. 6c, d and Table 5, after ball-milling, an obvious particle size decrement can be seen in M5 and M20 samples due to high-energy ball-milling. This energy is responsible for crystallite size reduction and lattice strain enhancement which can be measured from XRD patterns and Williamson–Hall equation (Table 5). Also, Fig. 6c, d displays semi-spherical particles with more homogeneous distribution due to ball-milling. Comparison of M5 and M20 micrographs, with respect to Table 5, exhibits that prolonged milling had no significant influence on further particle size decrement, and the main change made by longer milling was an increase in the homogeneity of particles. It is notable that the maximum milling time of 20 h partly moderated the cold welding phenomenon and, consequently, the agglomeration of MgH₂ particles, which is highly prevalent in the MgH₂ milling process [12, 19]. The micrograph of as-received PMMA can be seen in Fig. 6b which exhibits very smaller particles compared with as-received MgH₂. Upon the comparison of Fig. 6b with e, f (related to M5P and M20P samples, respectively), it can be observed that mechanical milling for 2 h had no discernible effect on the morphology and size of particles. This phenomenon, which is reported in the PMMA milling process by Karthick et al. [38], is due to its inherent high stiffness [39]. Figure 6e, f exhibits the good coverage of milled MgH₂ particles by PMMA which is predictable because of the high mass fraction of polymer in M5P and M20P samples. The marked areas demonstrate MgH₂ agglomerates which are sufficiently covered by PMMA particles, so it can be expected that air stability enhancement would be seen for M5P and M20P samples (Fig. 2).

The FTIR spectra of M5P and M20P and PMMA powders can be observed in Fig. 3. This figure shows all Mg–H bonds' vibrations for M5P and M20P between the wavenumber of 1500 to 500 1/cm which is called the fingerprint area [28, 40]. The PMMA spectrum displays two peaks in the wavenumber range of 3700 to 3200 1/cm which are attributed to the stretching vibrations of the O–H bond [41]. In both M5P and M20P spectra, these O–H bonds' peaks are transformed into a one broadened peak, and this change may be related to a new O–H interaction between MgH₂ and PMMA [31]. In the wavenumber range of 3100 to 2700 1/cm, the PMMA spectrum shows three peaks of C–H bond vibrations. These peaks in M5P and M20P samples were changed probably because of a change in the vibration behavior of this bond affected by mechanical milling. Comparison of PMMA and MgH₂–PMMA spectra in 1000 to 500 1/cm wavenumber range shows that the peaks of PMMA in that range, assigned to out of plane O–H bonding [42] and C–H stretching [43], do not have any distinguishable influence on MgH₂–PMMA spectra, and Mg–H peaks are more

Fig. 1 XRD patterns of **a** MNB (as received MgH_2), **b** M5, **c** M20, **d** M5P and **e** M20P samples (see Table 1 for abbreviations)

detectable in that range. Accordingly, it can be concluded that the outcome of mechanical milling of MgH_2 and PMMA was not only a physical mixing of the two materials, but also some new interactions and possibly bonds formed due to the milling process. This phenomenon should be further investigated in future studies.

TGA analysis

The results of TGA experiments related to the weight loss percentage (dehydrogenation) performance of all samples are given in Table 1. The TGA diagrams of M5, and M20 samples are illustrated in Fig. 4. This figure indicates that, by mechanical milling for 5 and 20 h, the weight loss

Table 5 The results of TGA analysis on the M5P, M2N5P, and M5N5P samples

Sample	Decrease in wt.% of MgH ₂ Up to 300 °C (max = 7.6%)	Decrease in wt.% MgH ₂ up to 300 °C + 15-min holding (max = 7.6%)	Desorption onset Temperature (°C)
M5P	3.25	6.21	180
M2N5P	4.49	7.00	180
M5N5P	4.64	7.11	180

percentage up to 450 °C is increased from 2.46 for M5 to 3.37 wt.% for M20. The initial temperature of dehydrogenation is also decreased from 421 °C for MNB to 405 and 370 °C for M5 and M20 samples, respectively. Based on Table 5, particle size decrement and structural defects increment, made by mechanical milling, shortened the diffusion paths of H atoms in the disordered MgH₂ structure and enhanced the dehydrogenation kinetics [44].

Kizilduman et al. [45] investigated the thermal decomposition process of PMMA and reported that the weight loss of PMMA at temperatures of 275, 366, and 420 °C is ~ 5, 50, and 100%, in that order. The decomposition of PMMA has three initiation processes. The first process is initiation by weak linkages between 155 and 220 °C. The second one is initiation by labile chain ends (terminal bonds and unsaturation or initiator moieties) between 230 and 300 °C. The last one is the random chain scission of C–C bonds at the repeat unit over 330 °C. Afterwards, a radical is formed [45]. It is also reported that the flash point of PMMA is > 250 °C. During its ignition, the PMMA releases CO₂, H₂O, and CO, and does not release hydrogen [31]. Therefore, it seems that the reported weight loss of PMMA during heating is because of its decomposition.

Based on the mentioned results and our initial experiments, it seemed that it is practical to minimize PMMA destruction during TGA analysis and the dehydrogenation process for MgH₂–PMMA composites. The results of TGA analysis of as-received PMMA (Fig. 5 and Table 1) show that the weight loss of PMMA after heating up to 300 °C and then holding at this temperature for 15 min was 5.83% and 7.52%, respectively. All the TGA diagrams of MgH₂–PMMA composites in this study are depicted after the subtraction of TGA results of PMMA for an accurate investigation of MgH₂ dehydrogenation.

Figure 6 displays the TGA analysis of M5P and M20P samples. Comparison between TGA results of M5P with that of M5 sample demonstrates that the weight loss percentage of 5h milled powder increased from 2.46 at 450 °C in bare

MgH₂ sample to 3.25% at 300 °C and after 15-min holding at this temperature to 6.21% in the presence of PMMA. Therefore, the protection of MgH₂ by PMMA has successfully prevented the surface of MgH₂ particles from the formation of a MgO/Mg(OH)₂ layer. This is important because the formation of this passive layer can make H atoms' diffusion during the dehydrogenation process very difficult [46, 47]. Thus, air stability created in the composite by PMMA reduced MgO/Mg(OH)₂ layer formation and consequently improved the dehydrogenation kinetics of M5P and M20P samples. Using 80 wt.% of polymer decreased the theoretical desorption capacity of the composite, but the dehydrogenation performance of the embedded MgH₂ in PMMA bed significantly increased.

The effect of PMMA's presence on the dehydrogenation properties of the 20 h milled sample is quite similar to the M5 sample, with the only difference being that the dehydrogenation enhancement by adding PMMA to the 5 h milled sample is more notable compared to the 20-h milled one. This can be attributed to the partial agglomeration of particles in the M20P sample. This behavior can be verified by the results shown in Table 5. Evidently, the particle and crystallite size decrement and lattice strain increment for the M20P sample compared with M20 is moderate, while these structural changes are more intense for M5 and M5P samples.

The other significant influence of PMMA's presence on MgH₂ dehydrogenation performance is a remarkable reduction in initial desorption temperature from 405 °C for M5 to 180 °C for M5P, and from 370 °C for M20 to 175 °C for M20P sample. Thus, the confinement of MgH₂ by PMMA successfully protected the surface of hydride against oxidation and MgO/Mg(OH)₂ layer formation which behaves as a diffusion barrier against the mobility of H atoms during the dehydrogenation process [48]. Overcoming this diffusion obstacle needs temperature enhancement which is equal to the initial desorption temperature increment.

To investigate the influence of PMMA on MgH₂ air stability, the dehydrogenation performance of M5PA and M20PA samples exposed to air for 4 weeks are depicted in Fig. 7. It is observed that the dehydrogenation percentage of the M5P sample up to 300 °C decreased from 3.25 to 2.76% after air exposure. Also, the dehydrogenation percentage of the M5P sample decreased from 6.21 to 5.80% after holding these samples at 300 °C for 15 min. Furthermore, in both conditions, a slight increment of initial desorption temperature was recorded (from 180 to 184 °C for M5P and from 175 to 181 °C for M20P sample). Based on Fig. 2, the coverage of MgH₂ with PMMA was not complete. Therefore, it is expectable that the surface of MgH₂ would oxidize partially. This oxidation prevents the diffusion of

Fig. 2 SEM images of **a** MNB (as received MgH_2), **b** PMMA (as received), **c** M5, **d** M20, **e** M5P and **f** M20P samples (see Table 1 for abbreviation)

hydrogen molecules and decreased desorption capacity. The same behavior is observed for M20P and M20PA samples. It can be deduced from the drastic activation of milled MgH_2 and its high atmosphere sensibility that PMMA effectively enhanced the atmosphere stability of MgH_2 , while even non-activated MgH_2 is immediately oxidized in contact with air or any $\text{O}_2/\text{H}_2\text{O}$ containing atmosphere.

Effect of nickel catalyst

The catalytic effect of nickel on the improvement of MgH_2 dehydrogenation is well known and reported in many papers [4]. Therefore, the authors decided to investigate the simultaneous effect of adding Ni and confinement of MgH_2 with PMMA in this study. First, MgH_2 and Ni powder were

Fig. 3 FTIR spectra of PMMA (as received), M5P, and M20P samples (see Table 1 for abbreviation)

Fig. 4 TGA diagrams of M5, and M20 samples (see Table 1 for abbreviations)

milled for 5 h, and then the milled mixture was milled with PMMA for 2 h. Figure 8 and Table 2 show the effect of adding 2 (M2N5P) and 5 (M5N5P) wt.% nickel catalyst to the M5P sample. Results of TGA experiments revealed that the weight loss percentage up to 300 °C is 4.49 and 4.64 for 2 and 5 wt.% nickel added samples, in that order. Evidently, after holding these samples at 300 °C for 15 min, the weight loss percentage increased to 7.00 and 7.11 wt.% which are very close to the theoretical value (7.6 wt.% for pure MgH_2). This proximity to the theoretical value is

Fig. 5 TGA diagram of PMMA (as received) **a** up to 300 °C, **b** after 15-min holding at 300 °C

due to the simultaneous effect of mechanical milling and the addition of Ni catalyst. The free surfaces produced as a result of fracture of particles during mechanical milling are protected from oxidation by PMMA. Furthermore, the presence of a carbonyl group in the PMMA weakened the Mg–H bonds [31]. Nickel facilitates the hydrogen adsorption and decreases the activation energy for the reaction between hydrogen atoms on the surface of MgH_2 particles. The addition of Ni also increased the number of sites for magnesium nucleation on the surface of MgH_2 . The desorbed hydrogen atoms would also be adsorbed on the surface of the nickel catalyst and bond together on this surface (hydrogen spillover phenomenon).

It can be observed that the onset temperature of hydrogen desorption for both samples was 180 °C and the addition of nickel did not influence the onset temperature of hydrogen desorption. It is reported that adding catalyst influences the

Fig. 6 TGA diagrams of M5P and M20P samples at **a** 300 °C and **b** 15-min holding at 300 °C (see Table 1 for abbreviations)

kinetics of hydrogen desorption, and the enthalpy of this process does not change due to the addition of catalysts [14]. Table 2 shows that the onset temperature of desorption of all three samples in the same condition is equal. However, because of the kinetic effect of adding nickel catalyst, the decrease in weight percent of the catalyst-containing sample significantly improved as it reached the theoretical value in 5 wt.% containing nickel.

Conclusion

The results of this study were satisfying enough for introducing mechanical milling as a promising and effective method for the synthesis of metal hydride–polymer composites. The results can be summarized as follows:

1. SEM images demonstrated the good coverage of milled MgH_2 particles by PMMA due to the 2-h milling of the MgH_2 –PMMA mixture.

Fig. 7 The TGA analysis results of M5PA and M20PA samples **a** at 300 °C and **b** after 15-min holding at 300 °C (see Table 1 for abbreviation)

2. The results of TGA showed that the weight loss percentage of 5 h milled powder increased from 2.46 at 450 °C in bare MgH_2 sample to 3.25% at 300 °C, and after 15-min holding at this temperature, to 6.21% in the presence of PMMA.
3. The effect of PMMA presence on the dehydrogenation properties of the 20-h milled sample is quite similar to the 5-h milled one.
4. The initial desorption temperature decreased from 405 °C for the 5-h milled MgH_2 to 180 °C for the 5-h milled MgH_2 –PMMA mixture, and from 370 °C for the 20-h milled MgH_2 to 175 °C for the 20-h milled MgH_2 –PMMA sample. Both mechanical milling and confinement of MgH_2 by PMMA significantly improved the efficiency of hydrogen desorption from MgH_2 .
5. The dehydrogenation percentage of the 5-h milled MgH_2 –PMMA mixture up to 300 °C decreased from 3.25 to 2.76% after 4 weeks of air exposure. Also, the dehydrogenation percentage of the 5-h milled MgH_2 –

Fig. 8 Comparing the results of TGA analysis of M2N5P and M5N5P samples with M5P **a** at 300 $^{\circ}\text{C}$ and **b** after 15-min holding at 300 $^{\circ}\text{C}$ (see Table 1 for abbreviation)

PMMA sample decreased from 6.21 to 5.80% after holding these samples at 300 $^{\circ}\text{C}$ for 15 min. In both conditions, a slight increment of initial desorption temperature was recorded. Acceptable hydrogen desorption from MgH_2 –PMMA composite after 4 weeks of air exposure proved that the polymer bed was successful in enhancing MgH_2 air stability by protecting its surface against oxidation.

6. Addition of 2 and 5 wt.% nickel as the catalyst to the M5P sample improved the kinetics of the hydrogen desorption process as the weight loss percentage of this sample reached 7.00% and 7.11% after 15-min holding at 300 $^{\circ}\text{C}$, which was very close to its theoretical value.

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